# SITE QUALITY ASSURANCE PROJECT PLAN AND FIELD SAMPLING PLAN JEWETT WHITE LEAD SITE

**2000-2012, 2015 Richmond Terrace, Borough of Staten Island, Richmond County, New York, 10302**

**NON-TIME CRITICAL**

**Prepared By:**

**Removal Support Team 2**
**Weston Solutions, Inc.**
**Northeast Division**
**Edison, New Jersey 08837**

**DCN No.: RST 2-02-F-1398**
**Task Order No.: 18**
**EPA Contract No.: EP-W-06-072**

**September 2010**

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SOP No.: 2016 - Sediment Sampling
Innov-X Model X-50 Unit User's Manual
EPA Method 6200

## LIST OF ACRONYMS

| | |
|---|---|
| bgs | below ground surface |
| CLP | Contract Laboratory Program |
| COC | Chain-of-Custody |
| CRQL | Contract Required Quantitation Limit |
| DCN | Document Control Number |
| DESA | Division of Environmental Science and Assessment |
| DQI | Data Quality Indicator |
| DQO | Data Quality Objective |
| EPA | Environmental Protection Agency |
| ERT | Environmental Response Team |
| ESAT | Environmental Services Assistance Team |
| FPXRF | Field Portable X-Ray Fluorescence |
| ft | feet/foot |
| HASP | Health and Safety Plan |
| HSA | hollow-stem auger |
| HSO | Health and Safety Officer |
| LCSS | Laboratory Control Sample, Soil |
| LCSW | Laboratory Control Sample, Water |
| µg/L | micrograms per liter |
| mg/kg | milligrams per kilogram |
| MPC | measurement performance criteria |
| MS/MSD | Matrix Spike/Matrix Spike Duplicate |
| NYSDEC | New York State Department of Environmental Conservation |
| OSC | On-Scene Coordinator |
| OSHA | Occupational Safety and Health Administration |
| OSWER | Office of Solid Waste and Emergency Response |
| PARCCS | Precision, Accuracy, Representativeness, Completeness, Comparability, Sensitivity |
| PQO | project quality objectives |
| PRP | Potentially Responsible Party |
| PVC | polyvinyl chloride |
| QA | Quality Assurance |
| QAPP | Quality Assurance Project Plan |
| QAO | Quality Assurance Officer |
| QA/QC | Quality Assurance/Quality Control |
| QC | Quality Control |

## LIST OF ACRONYMS
## (concluded)

| | |
|---|---|
| RAS | Regular Analytical Services |
| RL | reporting limit |
| RPD | Relative Percent Difference |
| RPM | Remedial Program Manager |
| RSCC | Regional Sample Control Coordinator |
| RST | Removal Support Team |
| SCOs | Soil Cleanup Objectives |
| SOP | Standard Operating Practice |
| SOW | Statement of Work |
| SPLP | Synthetic Precipitation Leaching Procedure |
| SPM | Site Project Manager |
| STR | Sampling Trip Report |
| TAL | Target Analyte List |
| TBD | to be determined |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TDD | Technical Direction Document |
| UFP | Uniform Federal Policy |

# CROSSWALK

The following table provides a "cross-walk" between the QAPP elements outlined in the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP Manual), the necessary information, and the location of the information within the text document and corresponding QAPP Worksheet. Any QAPP elements and required information that are not applicable to the project are circled.

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## QAPP Worksheet #1: Title and Approval Page

**Title:** Site Quality Assurance Project Plan
**Site Name/Project Name:** Jewett White Lead Site
**Site Location:** Staten Island, New York
**Revision Number:** 04
**Revision Date:**

Weston Solutions, Inc
**Lead Organization**

Joseph Schmidl, PG, CWS
1090 King Georges Post Road, Suite 201
Edison, NJ 08837
Email: Joseph.Schmidl@WestonSolutions.com

**Preparer's Name and Organizational Affiliation**

Joseph Schmidl, PG, CWS

23 October 2010
**Preparation Date (Day/Month/Year)**

Site Project Manager:
Signature
Joseph Schmidl, PG, CWS/Weston Solutions, Inc.
**Printed Name/Organization/Date**

QA Officer/Technical Reviewer:
Signature
Smita Sumbaly/Weston Solutions, Inc.
**Printed Name/Organization/Date**

EPA Region 2 On-Scene Coordinator (OSC):
Signature
Kimberly Staiger/EPA Region 2
**Printed Name/Organization/Date**

EPA Region 2 Quality Assurance Officer (QAO):
Signature

**Printed Name/Organization/Date**

Document Control Number: RST 2-02-1398

## QAPP Worksheet #2
## QAPP Identifying Information

**Site Name/Project Name**: Jewett White Lead Site
**Site Location**: 2000-2012 Richmond Terrace, Staten Island, Richmond County, NY 10302
**Operable Unit**: 00
**Title:** Quality Assurance Project Plan
**Revision Number:** 00
**Revision Date:**

1. **Identify guidance used to prepare QAPP:**
   Uniform Federal Policy for Quality Assurance Project Plans. Refer to CLP Methods.

2. **Identify regulatory program:** EPA Region 2

3. **Identify approval entity:** EPA Region 2

4. **Indicate whether the QAPP is a generic or a Site-specific QAPP.**

5. **List dates of scoping sessions that were held:** 7 July 2010

6. **List dates and titles of QAPP documents written for previous site work, if applicable:**

   *Site Quality Assurance Project Plan – Jewett White Lead Company Site*,
   DCN: RST-2-F-0755, 10 December 2008.

   *Final Quality Assurance Project Plan – Jewett White Lead Company Site*,
   DCN: RST-2-F-1214, 15 December 2009.

7. **List organizational partners (stakeholders) and connection with lead organization:** None

8. **List data users:**
   EPA Region 2 (see Worksheet #4 for individuals)

9. **If any required QAPP elements and required information are not applicable to the project, then provide an explanation for their exclusion below:**

   None excluded

10. **Document Control Number:**
    RST 2-02-1398

## QAPP Worksheet #3: Distribution List

**[List those entities to which copies of the approved QAPP, subsequent QAPP revisions, addenda, and amendments are sent]**

| QAPP Recipient | Title | Organization | Telephone Number | Fax Number | E-mail Address | Document Control Number |
|---|---|---|---|---|---|---|
| Kimberly Staiger | EPA, On-Scene Coordinator | EPA Region 2 | (732) 452-6415 | (732) 906-6182 | Staiger.Kimberly@epa.gov | RST 2-02-1398 |
| Joseph Schmidl, PG, CWS | Site Project Manager, RST 2, ID/IQ staff | Weston Solutions, Inc. | (603) 656-5461 | (603) 656-5401 | Joseph.Schmidl@WestonSolutions.com | RST 2-02-1398 |
| Jennifer Sy | HSO, RST 2 | Weston Solutions, Inc. | (732) 585-4411 | (732) 225-7037 | Jennifer.Sy@WestonSolutions.com | RST 2-02-1398 |
| Smita Sumbaly | QA Officer, RST 2 | Weston Solutions, Inc. | (732) 585-4410 | (732) 225-7037 | S.Sumbaly@WestonSolutions. com | RST 2-02-1398 |
| Site TDD File | RST 2 Site TDD File | Weston Solutions, Inc. | - | - | - | - |

## QAPP Worksheet #4: Project Personnel Sign-Off Sheet

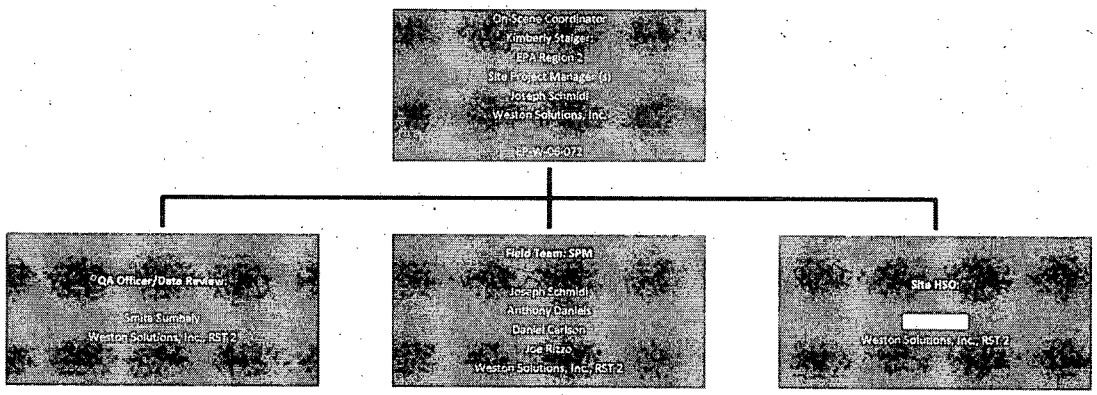
**[Copies of this form signed by key project personnel from each organization to indicate that they have read the applicable sections of the QAPP and will perform the tasks as described; add additional sheets as required. Ask each organization to forward signed sheets to the central project file.]**

**Organization:** Weston Solutions, Inc.

| Project Personnel | Title | Telephone Number | Signature | Date QAPP Read |
|---|---|---|---|---|
| Kimberly Staiger | EPA Region 2, On-Scene Coordinator | (732) 452-6415 | | |
| Joseph Schmidl, PG, CWS | Site Project Manager, RST 2 | (603) 656-5461 | | |
| Smita Sumbaly | QAO, RST 2 | (732) 585-4410 | | |
| Jennifer Sy | HSO, RST 2 | (732) 585-4411 | | |
| Anthony Daniels | Field Personnel, RST 2 | (732) 585-4447 | | |
| Daniel Carlson | Field Personnel, RST 2 | (732) 417-5863 | | |
| Scott Snyder | Field Personnel, RST 2 | (732) 417-5812 | | |
| Joe Rizzo | Field Personnel, RST 2 | (732) 417-5856 | | |

## QAPP Worksheet #5: Project Organizational Chart

Identify reporting relationship between all organizations involved in the project, including the lead organization and all contractor and subcontractor organizations. Identify the organizations providing field sampling, on-site and off-site analysis, and data review services, including the names and telephone numbers of all project managers, project team members, and/or project contacts for each organization.




**Acronyms:**

QA: Quality Assurance
SPM: Site Project Manager
HSO: Health & Safety Officer
TBD: To be determined

## QAPP Worksheet #6: Communication Pathways

| Communication Drivers | Responsible Entity | Name | Phone Number | Procedure |
|---|---|---|---|---|
| Point of contact with EPA OSC | Site Project Manager, Weston Solutions, Inc., RST 2 | Joseph Schmidl | 603-656-5461 | All technical, QA and decision-making matters in regard to the project (verbal, written or electronic) |
| Adjustments to QAPP | Site Project Manager, Weston Solutions, Inc., RST 2 | Joseph Schmidl | 603-656-5461 | QAPP approval dialogue |
| Health and Safety On-Site Meeting | Site Project Manager, Weston Solutions, Inc., RST 2 | Joseph Schmidl | 603-656-5461 | Explain Site hazards, personnel protective equipment, hospital location, etc. |

OSC: On-Scene Coordinator

## QAPP Worksheet #7: Personnel Responsibilities and Qualifications Table

| Name | Title | Organizational Affiliation | Responsibilities | Education and Experience Qualifications |
|---|---|---|---|---|
| Kimberly Staiger | EPA On-Scene Coordinator | EPA, Region 2 | All project coordination, direction and decision making. | NA |
| Joseph Schmidl | Site Project Manager, RST 2 | Weston Solutions, Inc. | Implementing and executing the technical, QA and health and safety during sampling event and sample management. | 20 years experience* |
| Scott Snyder | Field Personnel, RST 2 | Weston Solutions, Inc. | HSO, Sample management | 12 years experience* |
| Daniel Carlson | Field Personnel, RST 2 | Weston Solutions, Inc. | Sample collection | 1 year experience* |
| Anthony Daniels | Field Personnel, RST 2 | Weston Solutions, Inc. | Sample collection | 1 year experience* |
| Joe Rizzo | Field Personnel, RST 2 | Weston Solutions, Inc. | Sample collection | 1 year experience* |

*All RST 2 members, including subcontractor's resumes are in possession of RST 2 Program Manager, EPA Project Officer and Contracting officers.
NA = not applicable

## QAPP Worksheet #8: Special Personnel Training Requirements Table

| Project Function | Specialized Training By Title or Description of Course | Training Provider | Training Date | Personnel / Groups Receiving Training | Personnel Titles / Organizational Affiliation | Location of Training Records / Certificates1 |
|---|---|---|---|---|---|---|
| QAPP Training | This training is presented to all RST 2 personnel to introduce the provisions, requirements, and responsibilities detailed in the UFP QAPP. The training presents the relationship between the site-specific QA Project Plans (QAPPs), SOPs, work plans, and the Generic QAPP. QAPP refresher training will be presented to all employees following a major QAPP revision. | Weston Solutions, Inc., QAO | As needed | All RST 2 field personnel upon initial employment and as refresher training | Weston Solutions, Inc. | Weston Solutions, Inc., EHS Database |
| Health and Safety Training | Health and safety training will be provided to ensure compliance with Occupational Safety and Health Administration (OSHA) as established in 29 CFR 1910.120. | Weston Solutions, Inc., HSO | Yearly at a minimum | All Employees upon initial employment and as refresher training every year | Weston Solutions, Inc. | Weston Solutions, Inc., EHS Database |
| Others | FORMS II Lite, Scribe, ICS 100 and 200, and Air Monitoring Equipment Trainings provided to all employees | Weston Solutions, Inc., QAO/Group Leader's | Upon initial employment and as needed | | | |
| | Dangerous Goods Shipping | Weston Solutions, Inc., HSO | Every 2 years | | | |

All team members are trained in the concepts and procedures in recognizing opportunities for continual improvement, and the approaches required to improve procedures while maintaining conformance with legal, technical, and contractual obligations.

*All RST 2 members, including subcontractor's certifications are in possession of RST 2 HSO.

## QAPP Worksheet #9: Project Scoping Session Participants Sheet

**Site Name/Project Name**: Jewett White Lead Site
**Site Location**: 2000-2012, 2015 Richmond Terrace, Staten Island, NY 10302
**Operable Unit**: 00
**Date of Session:** July 7, 2010
**Scoping Session Purpose:** To discuss questions, comments, and assumptions regarding technical issues involved with the project.

| Name | Title | Affiliation | Phone # | E-mail Address | *Project Role |
|---|---|---|---|---|---|
| Joseph Schmidl | Site Project Manager | Weston Solutions, Inc. | 603-656-5461 | Joseph.Schmidl@WestonSolutions.com | Site Project Management |
| Kimberly Staiger | EPA OSC | EPA Region 2 | 732-452-6415 | Kimberly.Staiger@epa.gov | OSC |
| Jennifer Sy | Group Leader | Weston Solutions, Inc. | 732-585-4411 | Jennifer.Sy@WestonSolutions.com | Group Leader |

**Comments/Decisions:** Four RST 2 members will conduct the sampling. At 2000-2012 Richmond Terrace, soil samples will be collected from a total of 26 test pits excavated using a backhoe. At 2015 Richmond Terrace, soil samples will be collected from a total of 25 locations using a direct-push unit. Soil samples will be collected from 1-ft depth intervals from the surface at each location, with the depth below ground surface (bgs) of each soil boring or test pit determined based on the extent of lead impacts documented by field screening for lead on-site using a field portable X-ray fluorescence (FPXRF) unit. Twenty of these soil samples will be submitted to CLP for confirmatory analysis for total Lead, as well as Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) Lead.

Five overburden monitoring wells will be installed on-site (three at 2000 and two at 2015 Richmond Terrace) using hollow-stem auger (HSA) drilling methods. Each well will be developed and surveyed for location and elevation. Following equilibration, groundwater samples will be collected using low-flow methodology and submitted to CLP for total Lead analysis. Additional overburden monitoring wells may be installed in the future.

Up to five collocated sediment/surface water samples will be collected from storm sewer outfalls adjacent to the Site. The samples will be submitted to CLP for total Lead analysis.

**Action Items:** RST 2 will prepare the UFP-QAPP, submit the Analytical Request Form, and prepare for the sampling event. EPA will provide the UFP-QAPP to property owners and obtain site access

**Consensus Decisions:** Samples will be collected for definitive data. Sampling will be conducted during mid-September 2010.

## QAPP Worksheet #10: Problem Definition

### PROBLEM DEFINITION

EPA Region 2 has requested that RST 2 collect additional environmental data from the Jewett White Lead Site to support an Engineering Evaluation/Cost Analysis (EE/CA) of the historic footprint of the former Jewett White Lead Company facility and extent of contamination, which includes the 1-acre parcel of land at 2000-2012 Richmond Terrace and the approximately 1.5-acre parcel of land at 2015 Richmond Terrace.

### SITE HISTORY/CONDITIONS

Historically, John Jewett & Sons White Lead Company operated a white lead manufacturing facility at the Site. John Jewett & Sons White Lead Company owned the Site from 1839 until April 3, 1890 when National Lead & Oil Company of New York ("National Lead") acquired the Site property. National Lead continued the manufacture of white lead, an additive found in lead-based paint and ceramics, at the Site until about 1943. A fire destroyed the plant's main building and storage house in 1920. On December 31, 1943, Moran Towing Corporation acquired the 2015 Richmond Terrace portion of the Site from National Lead. On May 31, 1946, National Lead sold the remaining parcel of land located at 2000 Richmond Terrace. Between 1949 and 1990 various businesses operated at 2000-2012 Richmond Terrace, including Sedutto's Ice Cream factory.

Currently, the portion of the Site located at 2000-2012 Richmond Terrace is being used to store construction equipment and materials from local construction projects. The portion of the Site located at 2015 Richmond Terrace is presently owned by the Moran Towing Corporation, an active tug boat facility.

On June 3, 2008, the Council of the City of New York submitted a written request to EPA to evaluate the Site for a possible cleanup. In December 2008, EPA and contractor representatives collected soil samples throughout the 2000-2012 Richmond Terrace property. Elevated levels of lead were found throughout most of the property, both laterally and with depth. Elevated levels of lead were identified in a small area of the sidewalk on Richmond Terrace, demonstrating that lead contaminated soil had migrated from the Site onto the adjacent sidewalk during heavy rain events.

On 15 June 2009, EPA collected 14 surficial soil samples, some of which were identified as "grit", from portions of the 2015 Richmond Terrace property where exposed soil was present or where the concrete and asphalt appeared to be in disrepair. Elevated levels of lead were found to be in the surface soils, with the highest levels of lead present in the surface soils and grit immediately adjacent the Richmond Terrace sidewalk.

EPA has determined that an immediate cleanup is needed to address the potential for soil contamination to migrate offsite due to the current use of the Site.

RST 2 conducted an off-site reconnaissance on 7 July 2010, to assess access and potential barriers to fieldwork at the Site.

**QAPP Worksheet #10: Problem Definition (continued)**

**PROJECT DESCRIPTION**

During the Scoping Meeting, EPA indicated that soil, groundwater, sediment, and surface water data gaps will be eliminated by the collection of additional environmental samples. RST 2 has been tasked to collect soil samples from the two properties (2000-2012 and 2015 Richmond Terrace) that comprise the Site to better document existing soil conditions and to estimate the extent of soil that will need to be removed from the Site. RST 2 will collect soil samples from a total of 51 locations selected by RST 2 and EPA based on grid pattern. Soil samples will be collected from each of these locations at 1 foot intervals from the surface to a depth to be determined at each location, based on the extent of lead impacts or the depth of the water table, whichever is shallower. All soil samples will be screened for lead onsite using a FPXRF unit, and seven duplicate sample analyses will be performed. 10% of soil samples will be submitted to CLP for confirmatory analysis for total Lead, as well as TCLP and SPLP Lead. One MS/MSD and one field duplicate soil samples will be submitted to CLP.

Five overburden monitoring wells will be installed (three at 2000-2012, and two at 2015 Richmond Terrace) using HSA drilling methods. Soil samples will be collected from each of the well locations at 1 foot intervals to the depth of the water table. Soil samples from the depth interval intersecting the water table will be submitted to CLP for confirmatory analysis for total Lead, as well as TCLP and SPLP Lead. Each well will be developed and surveyed for location and elevation. Following equilibration, groundwater samples will be collected using low-flow methodology and submitted to CLP for total Lead analysis. One MS/MSD and field duplicate groundwater sample will be submitted to CLP. Based on the validated analytical results, additional overburden monitoring wells may be required, and will be installed during a second-phase of investigation.

As-built plans for the storm sewer system surrounding the Site will be obtained from local authorities and reconnoitered to identify potential sediment/surface water sample locations. Up to ten collocated sediment/surface water samples will be collected from storm sewers or their outfalls adjacent to the Site, as well as the Kill Van Kull. Sediment and surface water samples collected from the Kill Van Kull will be collected using a ponar sampler deployed from an EPA boat. The samples will be submitted to CLP for total Lead analysis. One MS/MSD and field duplicate sediment and surface water sample will be submitted to CLP.

EPA will request that the laboratory retain confirmatory soil and sediment samples for up to six months, to accommodate potential subsequent specialized analyses which may be required based on the validated analytical results.

Additional samples may be collected at the direction of the OSC based upon field conditions.

Ambient air monitoring will be conducted at upwind and downwind locations along the perimeter of the Site during intrusive activities to ensure no off-site migration of lead-impacted soils. Engineering controls, such as dust suppression via water spray, will be employed to eliminate dust generation. On-site personnel will wear personal dust monitors to document potential lead exposures.

## QAPP Worksheet #10: Problem Definition (concluded)

### PROJECT DECISION STATEMENTS

Site data will be evaluated in a Removal Action Alternatives Report. If the available environmental data are found to fully characterize lead impacts at the Site, then, removal options for soils which contain lead at concentrations above the EPA Soil Screening Value for commercial areas (800 mg/kg) will be evaluated in the Report. If the available environmental data are found to contain data gaps, then, additional multi-media sampling will be proposed to determine the extent of contamination.

## QAPP Worksheet # 11: Project Quality Objectives/Systematic Planning Process Statement

**Overall project objectives include:** Sampling will be conducted by RST 2 to identify/confirm the presence of contamination in site soils, groundwater, sediment, and surface water.

**Who will use the data?** Data will be used by EPA Region 2 OSC.

**What will the data be used for?** Data from this sampling event will be used to determine the nature and extent of soil, groundwater, sediment and surface water impacts, and will also be used to evaluate removal options for the Site.

**What types of data are needed?**
Matrix: Soil (Soil and Sediment); Aqueous (Groundwater, Surface Water, and Equipment Rinsate Blanks)
Type of Data: Screening and definitive data
Analytical Techniques: On-site screening analysis and off-site laboratory analyses
Parameters: Total Lead; TCLP Lead, and SPLP Lead (soil samples only)
Type of sampling equipments: Plastic bags, plastic scoops (soils and sediments); plastic tubing (groundwater)
Access Agreement(s): None. EPA will obtain access to 2000-2012 and 2015 Richmond Terrace.
Sampling locations: On-site and off-site

**How many data are needed?** In addition to available analytical results, soil samples at one foot intervals at up to 51 locations for a total of 204 samples (field screening results), with approximately 20 soil samples submitted to CLP. In addition, five groundwater samples and five sediment and surface water samples.

**How "good" does the data need to be in order to support the environmental decision?** Sampling/analytical measurement performance criteria for PARCCS parameters will be established. Refer to Worksheet #12, criteria for performance measurement for screening and definitive data.

**Where, when, and how should the data be collected/generated?** Two properties (2000-2012 and 2015 Richmond Terrace) have been selected for soil sampling. Soil sample locations will be based on a 50-ft grid on 2000-2012 Richmond Terrace and a 100-ft grid on 2015 Richmond Terrace, without bias. Sediment and surface water samples will be collected from storm water catch basins proximal to the site, the outfalls from the storm water drainage system, and The Kill Van Kull. The sampling event is scheduled to be conducted in early September 2010. Additional samples may be collected at the direction of the OSC based upon field conditions.

**Who will collect and generate the data?** The samples will be collected by Weston Solutions, Inc. Soil samples will be screened for lead by a Weston Solutions, Inc. FPXRF operator. Laboratory samples will be analyzed by EPA's DESA Laboratory and validated by EPA's Environmental Services Assistance Team (ESAT).

**QAPP Worksheet # 11: Project Quality Objectives/Systematic Planning Process Statement (concluded)**

**How will the data be reported?** Data will be reported by the assigned laboratories (Preliminary, Electronics, and Hard Copy format). The Site Project Manager will provide a Sampling Trip Report, Status Reports, Maps/Figures, Analytical Report, and Data Validation Report to the EPA OSC.

**How will the data be archived?** Electronic data deliverables will be archived in the database. CLP data will be archived in EPA's document control room.

## QAPP Worksheet #12: Measurement Performance Criteria Table
## Worksheet # 12A: Lead - Inorganics/RST 2 Field Screen Lead EPA Method 6200

**(UFP-QAPP Manual Section 2.6.2)**
Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQI), measurement performance criteria (MPC) and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

| | |
|---|---|
| **Matrix** | Soil |
| **Analytical Group** | Lead Field Screen by FPXRF |
| **Concentration Level** | (mg/kg) |

| Sampling Procedure[1] | Analytical Method/SOP[2] | Data Quality Indicators (DQIs) | Measurement Performance Criteria | QC Sample and/or Activity Used to Assess Measurement Performance | QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A) |
|---|---|---|---|---|---|
| | EPA Method 6200/ Innov-X Model X-50 FPXRF Unit User's Manual | Precision (field) | ≤20% RPD* | Field Duplicate | S & A |
| | | Accuracy (field) | No analyte > RL* | Standardization Blank | S & A |
| | | Precision (laboratory) | ≤20% RPD* | Duplicate Sample ** | A |
| | | Accuracy (laboratory) | 75–125%;<br>80–120 % | Standardization Blank | A<br>A |

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
*Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria): http://www.epa.gov/region02/qa/qa_documents/SOP%20HW02%20FINAL%20Rev-13-ILM05_3.pdf
**Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Duplicate Sample Criteria - (include absolute difference criteria)

## QAPP Worksheet #12: Measurement Performance Criteria Table
## Worksheet # 12B: TAL Metals - Inorganics/CLP ILMO5.4

**(UFP-QAPP Manual Section 2.6.2)**
Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQI), measurement performance criteria (MPC) and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

| | |
|---|---|
| **Matrix** | Soil (Soil, Sediment) |
| **Analytical Group** | Total Lead |
| **Concentration Level** | ICP-AES (mg/kg) |

| Sampling Procedure[1] | Analytical Method/SOP[2] | Data Quality Indicators (DQIs) | Measurement Performance Criteria | QC Sample and/or Activity Used to Assess Measurement Performance | QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A) |
|---|---|---|---|---|---|
| | ILM05.4 | Precision (field) | ≤ 35% RPD* | Field Duplicate | S & A |
| | | Accuracy (field) | No analyte > CRQL* | Field Blank | S & A |
| | | Precision (laboratory) | ≤ 35% RPD* | Duplicate Sample** | A |
| | | Accuracy (laboratory) | 75–125%; | Matrix Spike***; LCSS**** | A |

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
*Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria): http://www.epa.gov/region02/qa/qa_documents/SOP%20HW02%20FINAL%20Rev-13-ILM05_3.pdf
**Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Duplicate Sample Criteria
***Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Spike Sample Criteria
****Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for solid Laboratory Control Sample (LCSS) **Note: Control Limits established by USEPA for LCSS:** http://www.epa.gov/superfund/programs/clp/ilm5.htm

## QAPP Worksheet #12: Measurement Performance Criteria Table
## Worksheet # 12C: TCLP Metals - Inorganics/CLP EPA Method 1311 Extraction/ILMO5.4

**(UFP-QAPP Manual Section 2.6.2)**
Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQI), measurement performance criteria (MPC) and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

| | |
|---|---|
| **Matrix** | Soil (Soil) |
| **Analytical Group** | TCLP |
| **Concentration Level** | ICP-AES (mg/L) |

| Sampling Procedure[1] | Analytical Method/SOP[2] | Data Quality Indicators (DQIs) | Measurement Performance Criteria | QC Sample and/or Activity Used to Assess Measurement Performance | QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A) |
|---|---|---|---|---|---|
| | SW 846 Method 1311 TCLP Extraction and ILM05.4 | Precision (field) | ≤ 35% RPD* | Field Duplicate | S & A |
| | | Accuracy (field) | No analyte > CRQL* | Field Blank | S & A |
| | | Precision (laboratory) | ≤ 35% RPD* | Duplicate Sample** | A |
| | | Accuracy (laboratory) | 75–125%; | Matrix Spike***; LCSS**** | A |

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
*Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP – (include absolute difference criteria): http://www.epa.gov/region02/qa/qa_documents/SOP%20HW02%20FINAL%20Rev-13-ILM05_3.pdf
**Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Duplicate Sample Criteria
***Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Spike Sample Criteria
****Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for solid Laboratory Control Sample (LCSS) Note: Control Limits established by USEPA for LCSS: http://www.epa.gov/superfund/programs/clp/ilm5.htm

## QAPP Worksheet #12: Measurement Performance Criteria Table
## Worksheet # 12D: SPLP Metals - Inorganics/CLP EPA Method 1312 Extraction/ILMO5.4

**(UFP-QAPP Manual Section 2.6.2)**
Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQI), measurement performance criteria (MPC) and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

| | |
|---|---|
| **Matrix** | Soil (Soil) |
| **Analytical Group** | SPLP |
| **Concentration Level** | ICP-AES (mg/L) |

| Sampling Procedure[1] | Analytical Method/SOP[2] | Data Quality Indicators (DQIs) | Measurement Performance Criteria | QC Sample and/or Activity Used to Assess Measurement Performance | QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A) |
|---|---|---|---|---|---|
| | SW 846 Method 1312 SPLP Extraction and ILM05.4 | Precision (field) | ≤ 35% RPD* | Field Duplicate | S & A |
| | | Accuracy (field) | No analyte > CRQL* | Field Blank | S & A |
| | | Precision (laboratory) | ≤ 35% RPD* | Duplicate Sample** | A |
| | | Accuracy (laboratory) | 75–125%; | Matrix Spike***; LCSS**** | A |

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
*Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP – (include absolute difference criteria): http://www.epa.gov/region02/qa/qa_documents/SOP%20HW02%20FINAL%20Rev-13-ILM05_3.pdf
**Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Duplicate Sample Criteria
***Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Spike Sample Criteria
****Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for solid Laboratory Control Sample (LCSS) Note: Control Limits established by USEPA for LCSS: http://www.epa.gov/superfund/programs/clp/ilm5.htm

## QAPP Worksheet #12: Measurement Performance Criteria Table
## Worksheet # 12E: TAL Metals - Inorganics/CLP ILMO5.4

**(UFP-QAPP Manual Section 2.6.2)**
Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQI), measurement performance criteria (MPC) and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

| | |
|---|---|
| **Matrix** | Aqueous (Groundwater, Surface Water, Rinsate Blank) |
| **Analytical Group** | Total Lead |
| **Concentration Level** | ICP-AES (µg/L) |

| Sampling Procedure[1] | Analytical Method/SOP[2] | Data Quality Indicators (DQIs) | Measurement Performance Criteria | QC Sample and/or Activity Used to Assess Measurement Performance | QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A) |
|---|---|---|---|---|---|
| | ILM05.4 | Precision (field) | ≤20% RPD* | Field Duplicate | S & A |
| | | Accuracy (field) | No analyte > CRQL* | Field Blank | S & A |
| | | Precision (laboratory) | ≤20% RPD* | Duplicate Sample ** | A |
| | | Accuracy (laboratory) | 75–125%;<br>80–120 % | *** Matrix Spike;<br>LCSW**** | A<br>A |

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
*Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria):
http://www.epa.gov/region02/qa/qa_documents/SOP%20HW02%20FINAL%20Rev-13-ILM05_3.pdf
**Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Duplicate Sample Criteria - (include absolute difference criteria)
***Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for Spike Sample Criteria
****Reference USEPA CLP ILM05.4, Exhibit D of ICP-AES for aqueous Laboratory Control Sample (LCSW) Criteria w/exception of Ag and Sb
http://www.epa.gov/superfund/programs/clp/ilm5.htm

## QAPP Worksheet #12: Measurement Performance Criteria Table
## Worksheet # 12F: TAL Metals - Inorganics/NIOSH Method 7082

**(UFP-QAPP Manual Section 2.6.2)**
Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQI), measurement performance criteria (MPC) and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

| | |
|---|---|
| **Matrix** | Particulate (Dust Monitor Filter) |
| **Analytical Group** | Total Lead |
| **Concentration Level** | Flame AAS ($\mu g/m^3$) |

| Sampling Procedure[1] | Analytical Method/SOP[2] | Data Quality Indicators (DQIs) | Measurement Performance Criteria | QC Sample and/or Activity Used to Assess Measurement Performance | QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A) |
|---|---|---|---|---|---|
| | NIOSH 7082 | Precision (field) | ≤20% RPD | None | S & A |
| | | Accuracy (field) | No analyte > CRQL | None | S & A |
| | | Precision (laboratory) | ≤20% RPD* | None | A |
| | | Accuracy (laboratory) | 75–125%;<br>80–120 % | None | A<br>A |

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

## QAPP Worksheet #13: Secondary Data Criteria and Limitations Table

Any data needed for project implementation or decision making that are obtained from non-direct measurement sources such as computer databases, background information, technologies and methods, environmental indicator data, publications, photographs, topographical maps, literature files and historical data bases will be compared to the DQOs for the project to determine the acceptability of the data. Thus, for example, analytical data from historical surveys will be evaluated to determine whether they satisfy the validation criteria for the project and to determine whether sufficient data was provided to allow an appropriate validation to be done. If not, then a decision to conduct additional sampling for the site may be necessary.

| Secondary Data | Data Source (Originating Organization, Report Title, and Date) | Data Generator(s) (Originating Org., Data Types, Data Generation/ Collection Dates) | How Data May Be Used (if deemed usable during data assessment stage) | Limitations on Data Use |
|---|---|---|---|---|
| Previous Investigation Sampling Results | Data Reports, Sampling Trip Reports delivered to EPA. | EPA Region 2. 15 December 2008 (Sampling Report Data Presentation), 3 February 2009 (Sampling Trip Report), and USEPA-CLP Inorganic Analysis Data Sheets for samples received on 16 June 2009. | Data used to confirm soil and sediment contamination. | None. |

## QAPP Worksheet #14: Summary of Project Tasks

**Sampling Tasks**: Soil: Up to 104 soil samples will be collected from up to 25 test pits at 2000-2012 Richmond Terrace. Soil samples will be collected at each location at 1-ft depth intervals, beginning at the surface and extending to limit of lead impacts or the water table, whichever is shallower. In addition, soil samples will be collected at each monitoring well location at 1-ft depth intervals, beginning at the water table and extending to limit of lead impacts, or 7 ft below the water table, whichever is shallower. Up to 100 soil samples will be collected from up to 25 direct-push boring locations at 2015 Richmond Terrace. Four samples will be collected at each location at 1-ft depth intervals, beginning at the surface and extending to limit of lead impacts or the water table, whichever is shallower.

Groundwater: Installation, development, surveying, and sampling of five overburden monitoring wells (3 at 2000-2012 Richmond Terrace and 2 at 2015 Richmond Terrace).

Sediment and Surface Water: Up to ten collocated sediment/surface water samples will be collected from storm sewers or their outfalls adjacent to the Site, as well as the Kill Van Kull. Sediment and surface water samples collected from the Kill Van Kull will be collected using a ponar sampler deployed from an EPA boat. Sample locations will be based on the results of Site reconnaissance and available as-built plans for the storm sewer system surrounding the Site, and will be approved by the OSC.

**Analysis Tasks**: Field screening of 211 soil samples using FPXRF by EPA Method 6200
Total Lead – Soil and Aqueous – CLP ILMO5.4
TCLP Lead – Soil– SW 846 Method 1311 TCLP Extraction and CLP ILMO5.4
SPLP Lead – Soil– SW 846 Method 1312 SPLP Extraction and CLP ILMO5.4

**Quality Control Tasks:** QA/QC samples will include the collection of one duplicate and additional volume for one MS/MSD at the ratio of 1 per 20 samples and one rinsate blank per day.

**Data Management Tasks:** The data collected for the sampling activities will be organized, analyzed, and summarized in status and trip reports and other deliverables (e.g., analytical reports, final reports) that will be submitted to the OSC according to the Project Schedule. The reports will be prepared by the Project Manager and include appropriate data quality assessment. Standard methods and references will be used as guidelines for data reduction and reporting.

**Documentation and Records:** Field logbook, photodocumentation, sample labels, custody seals, chain of custody, sample logs, soil boring logs, well construction logs, test pit logs, etc.

All sample documents will be completed legibly, in ink. Any corrections or revisions will be made by lining through the incorrect entry and by initialing the error.

The following deliverables will be provided under this project:

Trip Report: A trip report will be prepared to provide a detailed accounting of what occurred during each sampling mobilization. The trip report will be prepared within 2 weeks of the last day of each sampling mobilization. Information will be provided on time of major events, dates, and personnel on-site (including affiliations).

Maps/Figures: Maps depicting site layout, contaminant source areas, and sample locations will be included in the trip report, as appropriate.

**QAPP Worksheet #14: Summary of Project Tasks (continued)**

Field Logbook: The field logbook is essentially a descriptive notebook detailing site activities and observations so that an accurate account of field procedures can be reconstructed in the writer's absence. The field logbook will be bound and paginated. All entries will be dated and signed by the individuals making the entries, and should include (at a minimum) the following:

1. Site name and project number
2. Name(s) of personnel on-site
3. Dates and times of all entries (military time preferred)
4. Descriptions of all site activities, site entry and exit times
5. Noteworthy events and discussions
6. Weather conditions
7. Site observations
8. Sample and sample location identification and description*
9. Subcontractor information and names of on-site personnel
10. Date and time of sample collections, along with chain of custody information
11. Record of photographs
12. Site sketches

* The description of the sample location will be noted in such a manner as to allow the reader to reproduce the location in the field at a later date.

Sample Labels: Sample labels will clearly identify the particular sample, and should include the following:

1. Site/project number.
2. Sample identification number.
3. Sample collection date and time.
4. Designation of sample (grab or composite).
5. Sample preservation.
6. Analytical parameters.
7. Name of sampler.

Sample labels will be written in indelible ink and securely affixed to the sample container. Tie-on labels can be used if properly secured.

Custody Seals: Custody seals demonstrate that a sample container has not been tampered with or opened. The individual in possession of the sample(s) will sign and date the seal, affixing it in such a manner that the container cannot be opened without breaking the seal. The name of this individual, along with a description of the sample packaging, will be noted in the field logbook.

**Assessment/Audit Tasks:** No performance audit of field operations is anticipated at this time. If conducted, performance and systems audits will be in accordance with the project plan.

**Data Review Tasks:** All CLP data will be validated by EPA Region 2 DESA/HWSB/ HWSS in accordance with latest SOW.

## QAPP Worksheet #15: Reference Limits and Evaluation Tables

**Matrix:** Soil (Soil)
**Analytical Group:** Field Screen Lead
**Concentration Level:** Low FPXRF

| Analyte | CAS Number | NYSDEC Restricted Use Soil Cleanup Objectives (mg/kg)* | | NYSDEC Unrestricted Soil Cleanup Objectives (mg/kg)** | EPA Restricted Use Soil Screening Value (mg/kg) | Project Quantitation Limit (mg/kg) | Analytical Method – EPA 6200 Quantitation Limits (mg/kg) |
|---|---|---|---|---|---|---|---|
| | | Residential | Commercial | | | | |
| Lead | 7439-92-1 | 400 | 1,000 | 63 | 800 | NS | 5 |

*New York State Department of Environmental Protection (NYSDEC) – SubPart 375-6.4, Restricted Use Soil Cleanup Objectives, 14 December 2006.
**New York State Department of Environmental Protection (NYSDEC) – SubPart 375-6.3, Unrestricted Use Soil Cleanup Objectives, 14 December 2006.
NS = Not Specified

**Matrix:** Soil (Soil, Sediment***)
**Analytical Group:** Target Analyte List Lead
**Concentration Level:** Low – ICP-AES

| Analyte | CAS Number | NYSDEC Restricted Use Soil Cleanup Objectives (mg/kg)* | | NYSDEC Unrestricted Soil Cleanup Objectives (mg/kg)** | EPA Restricted Use Soil Screening Value (mg/kg) | Project Quantiation Limit (mg/kg) | Analytical Method – SOM01.2 Quantitation Limits (mg/kg) |
|---|---|---|---|---|---|---|---|
| | | Residential | Commercial | | | | |
| Lead | 7439-92-1 | 400 | 1,000 | 63 | 800 | NS | 1. |

*New York State Department of Environmental Protection (NYSDEC) – SubPart 375-6.4, Restricted Use Soil Cleanup Objectives, 14 December 2006.
**New York State Department of Environmental Protection (NYSDEC) – SubPart 375-6.3, Unrestricted Use Soil Cleanup Objectives, 14 December 2006.
***For the purposes of this evaluation, and based on the lack of environmental targets, sediment lead concentrations will be compared to residential/commercial soil human health standards.
NS = Not Specified

## QAPP Worksheet #15: Reference Limits and Evaluation Tables (concluded)

**Matrix:** Aqueous (Groundwater, Surface Water, Rinsate*)
**Analytical Group:** Target Analyte List Lead
**Concentration Level:** Low – ICP-AES

| Analyte | CAS Number | NYSDEC Groundwater Quality Standards **(µg/L) | NYS Surface Water Quality Standards*** (µg/L) | Project Quantiation Limit (µg/L) | Analytical Method – ILMO5.4 ICP-AES Quantitation Limits (µg/L) |
|---|---|---|---|---|---|
| Lead | 7439-92-1 | 25 | 50 | NS | 10 |

* Rinsate blanks and will be collected to assess the efficacy of the decontamination process.
** Based on NYSDEC Part 703 Water Quality Standards for human health for groundwater used as a drinking water source.
*** Based on NYSDEC Part 703 Water Quality Standards for human health for surface water used as a drinking water source.
NS = Not Specified

## QAPP Worksheet #16: Project Schedule/Timeline Table

| Activities | Organization | Dates | | Deliverable | Deliverable Due Date |
|---|---|---|---|---|---|
| | | Anticipated Date(s) of Initiation | Anticipated Date of Completion | | |
| Preparation of QAPP | RST 2 Contractor Site Project Manager | Prior to sampling date | 30 July 2010 | QAPP | 30 July 2010 |
| Review of QAPP | RST 2 Contractor QAO and/or Group Leader | Prior to sampling date | 4 August 2010 | Approved QAPP | 4 August 2010 |
| Preparation of Health and Safety Plan | RST 2 Contractor Site Project Manager | Prior to sampling date | 6 August 2010 | HASP | 30 August 2010 |
| Procurement of Field Equipment | RST 2 Contractor Site Project Manager and/or Equipment Officer | Prior to sampling date | 27 August 2010 | NA | NA |
| Laboratory Request | RST 2 Contractor Site Project Manager and/or QAO | Prior to sampling date | 6 August 2010 | CLP Request Form | NA |
| Field Reconnaissance/Access | RST 2 Contractor Site Project Manager; or EPA Region 2 OSC | Prior to sampling date | 7 July 2010 | Access Agreement(s) | 27 August 2010 |
| Collection of Field Samples | RST 2 Contractor Site Project Manager | 6 September 2010 | 10 September 2010 | Sampling Trip Report | 24 September 2010 |
| Laboratory Electronic Data Received | EPA Region 2 DESA | 13 September 2010 | 24 September 2010 | Preliminary Data | 24 September 2010 |
| Laboratory Package Received | EPA Region 2 DESA | 13 September 2010 | 1 October 2010 | Laboratory Data Package | 1 October 2010 |
| Validation of Laboratory Results | EPA Region 2 DESA | 4 October 2010 | 22 October 2010 | Data Validation Report | 22 October 2010 |
| Data Evaluation/ Preparation of Final Report | RST 2 Contractor Site Project Manager | TBD | TBD | Final Report | TBD |

## QAPP Worksheet #17: Sampling Design and Rationale

**Soil Sampling:** RST 2 will collect up to 204 soil samples and 10 duplicate samples from up to 51 locations at the Site. All sampling will be conducted by RST 2, under the direction of the EPA OSC. The soil/aqueous samples will be collected for Total Lead analysis. These locations include 26 test pits to be excavated at 2000-2012 Richmond Terrace, designed to in-fill the existing 100-ft sampling grid, to result in 50-ft soil sample spacing, and 25 direct-push sample locations at 2015 Richmond Terrace, arranged in a 100-ft grid spacing. In the event that direct-push sampler refusal prevents sample collection to the required depth at 2015 Richmond Terrace, HAS drilling techniques will be employed to obtain the samples. In combination with existing soil data, the resultant dataset should provide adequate coverage to define the nature and extent of lead impacts associated with the Site. This sampling design is based on information currently available and may be modified onsite in light of field-screening results and other acquired information.

Soil sampling activities will be conducted in accordance with guidelines outlined in EPA/ERT Soil Sampling SOP #2012. Soil samples will be collected at up to 51 locations on Site, to the depth where lead impacts from the Site cease. Each test pit or soil core will be logged to characterize soil type, color, moisture, and other distinctive features. Soil samples will be collected from test pits or soil cores using disposable plastic tools, with grab samples being collected from each 1-foot depth interval at each location. At 2000-2012 Richmond Terrace, test pits will initially be sampled from the surface to 4 ft bgs. If FPXRF soil lead screening results indicate lead impacts (soil lead concentrations greater than 800 mg/kg) at 3 to 4 ft bgs, deeper soil samples will be collected, to the depth of the water table, whichever is shallower. At 2015 Richmond Terrace, the four initial soil boring sampling depths will be 0 to 1 ft., 1 to 2 ft., 2 to 3 ft., and 3 to 4 ft bgs. If FPXRF soil lead screening results indicate lead impacts (soil lead concentrations greater than 800 mg/kg) at 3 to 4 ft bgs, deeper soil samples will be collected, to the depth of the water table, if necessary. In addition, soil samples will be collected at each monitoring well location at 1-ft depth intervals, beginning at the water table and extending to limit of lead impacts (soil lead concentrations greater than 800 mg/kg), or 7 ft below the water table, whichever is shallower. Soils samples will be placed into 12-ounce polyethylene bags.

Field screening for lead in soil will be performed using FPXRF technology on-site. FPXRF sample analyses and handling will be conducted in accordance with the Innov-X Model X-50 FPXRF Unit User's Manual and EPA Method 6200 (see Attachment B). The samples will be homogenized within their polyethylene bag and analyzed for lead using the FPXRF three times. Organic debris and gravel will be removed from the sample before homogenization. Each XRF sample screening interval will last 30 seconds. The three results will be averaged to determine the lead concentration in the sample. Duplicate samples for FPXRF analysis will be split from the field sample following homogenization and analyzed separately. The FPXRF analysis results for lead will be logged electronically and recorded in the site logbook. Following FPXRF analyses, the soil samples will be cooled to 4°C and held until FPXRF analysis is complete for the Site.

**QAPP Worksheet #17: Sampling Design and Rationale (continued)**

Following FPXRF analysis, RST will select 20 of the 204 FPXRF samples and one of the FPXRF duplicate samples for confirmatory total Lead analysis. Samples will be selected to represent the range of soil types and FPXRF Total Lead analytical results noted at the Site, and will be approximately evenly distributed between samples from 2000-2012 and 2015 Richmond Terrace. Soil from each polyethylene sample bag will be placed into an 8-ounce amber glass jar with Teflon-lined septum cap, then labeled and sealed according to CLP protocols. EPA will request that the laboratory retain confirmatory samples for up to six months, to accommodate potential subsequent specialized analyses which may be required based on the validated analytical results.

**Sediment:** Sediment will be collected from up to ten or more locations where runoff from the Site appears to travel or collect, including swales, ditches, storm sewers, storm water outfalls, and the Kill Van Kull. Sample locations will be based on the results of Site reconnaissance and available as-built plans for the storm sewer system surrounding the Site, and will be approved by the OSC. Sediment samples will be collocated with surface water samples, where possible, and collected following surface water sample collection, in accordance with EPA/ERT 4 Sediment Sampling SOP# 2016. Sediment will be described to characterize soil type, color, moisture, and other distinctive features. Sediment samples will be homogenized in place and collected using disposable plastic tools directly into 8-ounce amber glass jars with Teflon-lined septum caps, then labeled and sealed according to CLP protocols. The sediment samples will be collected for Total Lead analysis. EPA will request that the laboratory retain sediment samples for up to six months, to accommodate potential subsequent specialized analyses which may be required based on the validated analytical results.

**Groundwater:** Five overburden groundwater monitoring wells will be installed using hollow-stem auger techniques, with three of the wells installed at 2000-2012 Richmond Terrace at previous soil sample locations A-4, B-2, and E-1, and the remaining two wells installed in the western and southern corners of 2015 Richmond Terrace. The wells will be constructed of 2-inch diameter Schedule 40 polyvinyl chloride (PVC), with 10-ft, 0.010-inch slotted, PVC well screen. The well annulus will be filled with a size 0 silica sand filter pack to 1 ft above the top of the well screen, a 2-ft bentonite seal, and cement/bentonite grout to the ground surface. Each well screen will be set to intercept the top of the water table, with approximately 3 ft of screen above the top of the water table. Each well will be completed with a 4-inch protective, flush-mount casing, and will be fitted with a lockable riser plug. No less than 24 hours following installation, each well will be developed by surging and pumping to remove fines from the filter pack to ensure a good hydraulic connection with the water table. Development water will be discharged to the ground surface. Wells will be surveyed for elevation (to the nearest 0.01 ft) following installation.

**QAPP Worksheet #17: Sampling Design and Rationale (continued)**

No less than two weeks following well installation, each well will be sampled for total Lead, using EPA's low-flow methodology, according to groundwater sample guidelines outlined in EPA/ERT 4 Groundwater Sampling SOP# 2007. Each will be purged using a peristaltic pump using Teflon-lined polyethylene tubing until groundwater parameters (measured using a flow through cell) stabilize. Purge water will be discharged to the ground surface, and the flow-through cell will be disconnected prior to sample collection. Groundwater samples will be collected using the same pump and tubing into 1-liter polyethylene bottles with Teflon-lined septum caps, pre-preserved with nitric acid, then labeled and sealed according to CLP protocols. The groundwater samples will be collected for Total Lead analysis.

**Surface Water:** Surface water will be collected from up to ten locations where runoff from the Site appears to travel or collect. Surface water samples will be collocated with sediment samples, where possible, and collected before sediment sample collection, in accordance with EPA/ERT 4 Surface Water Sampling SOP# 2013. Where sufficient surface water depth is present, surface water parameters will be measured in situ prior to sample collection. Surface water samples will be collected directly into 1-liter polyethylene bottles with Teflon-lined septum caps pre-preserved with nitric acid, then labeled and sealed according to CLP protocols. The surface water samples will be collected for Total Lead analysis.

**Rinsate Blanks:** Rinsate blank samples will be collected for each matrix/collection technique at a rate of 1 per day. Soil and sediment sample rinsate blanks will include a disposable plastic scoop; groundwater rinsate blanks will include a section of Teflon-lined polyethylene tubing. It is anticipated that surface water samples will be collected directly into sample containers, so no rinsate blank will be required. The aqueous samples will be collected for Total Lead analysis.

## QAPP Worksheet #17: Sampling Design and Rationale (concluded)

**Decontamination:** All reusable sampling equipment (i.e., soil sample core barrels and cutting shoes, groundwater monitoring equipment) involved in field-sampling activities will be decontaminated in accordance to EPA/ERT SOP #2006 prior to and subsequent to sampling, as well as between sampling locations. Decontamination of sampling equipment will be conducted as follows:

1. Alconox detergent and potable water scrub.
2. Potable water rinse.
3. Deionized water rinse.
4. 10% Nitric Acid rinse.
5. Deionized water rinse.
6. Deionized water rinse and air dry.
7. Wrap or cover exposed ends of sampling equipment with aluminum foil (shiny side out) for transport and handling.

Decontamination of excavation/drilling equipment (i.e., backhoe, drill rig, hollow-stem augers) will be conducted as follows:

1. Pressure washing using potable water.
2. Potable water rinse.
3. Deionized water rinse and air dry.

The following laboratories will provide the analyses indicated:

| Lab Name/Location | Sample Type | Parameters |
|---|---|---|
| DESA | Soil and Aqueous | Total Lead |
| DESA | Soil | TCLP Lead and SPLP Lead |
| EMSL Analytical | Particulate | Total Lead |

Refer to Worksheet #21 for QA/QC samples, sampling methods and SOP.

## QAPP Worksheet #18: Sampling Locations and Methods/SOP Requirements Table

| Matrix | Sampling Location(s) | Units | Analytical Group(s) | Concentration Level | No. of Samples (identify field duplicates) | Sampling SOP Reference | Rationale for Sampling Location |
|---|---|---|---|---|---|---|---|
| Soil | 25 Test Pit locations* | mg/kg | Lead (field screen), total Lead | Low | 100 samples plus 5 duplicates | EPA ERT SOP No.: 2012 | Characterization of soil lead concentrations at 2000-2012 Richmond Terrace property |
| | 26 direct-push sample locations | mg/kg | Lead (field screen), total Lead | Low | 104 samples plus 5 duplicates | EPA ERT SOP No.: 2012 | Characterization of soil lead concentrations at 2015 Richmond Terrace property |
| | 10 sediment locations | mg/kg | total Lead | Low | 5 samples plus 1 duplicate | EPA ERT SOP No.: 2016 | Characterization of sediment lead concentrations adjacent to Site |
| Aqueous | 5 overburden monitoring wells | µg/L | total Lead | Low | 5 samples plus 1 duplicate | EPA ERT SOP No.: 2007 | Characterization of lead in groundwater beneath Site |
| | 10 surface water locations | µg/L | total Lead | Low | 5 samples plus 1 duplicate | EPA ERT SOP No.: 2013 | Characterization of surface water lead concentrations adjacent to Site |
| | Rinsate Blanks | µg/L | total Lead | Low | 1 sample per day per matrix | EPA ERT SOP No.: 2006 | QA for Decontamination Process |
| Particulate | Site Perimeter and Personnel | µg/m$^3$ | total Lead | Low | 1 upwind, 2 downwind, personnel | | Health and Safety Compliance |

The website for EPA-ERT SOPs is: http://www.ert.org/mainContent.asp?section=Products&subsection=List
*Four samples will be collected at each location at depths of 0 to1 ft., 1 to 2 ft., 2 to 3 ft., and 3 to 4 ft.

## QAPP Worksheet #19: Analytical SOP Requirements Table

| Matrix | Number of Samples* | Analytical Group [Lab Assignment] | Concentration Level | Analytical and Preparation Method/SOP Reference | Sample Volume | Containers (number, size, and type) | Preservation Requirements | Maximum Holding Time (preparation/ analysis) |
|---|---|---|---|---|---|---|---|---|
| Soil* | 214 | Lead [field screen] | Low | ILM05.4 | 250 grams | (1) 12 oz. polyethylene bag | Cool to 4°C | 180 days |
| | 26 | Total Lead [CLP] | Low | ILM05.4 | 250 grams | (1) 8 oz. glass jar w/Teflon lined cap | Cool to 4°C | 180 days |
| | 21 | TCLP Lead [CLP] | Low | ILM05.4 | 250 grams | (1) 8 oz. glass jar w/Teflon lined cap | Cool to 4°C | 180 days |
| | 21 | SPLP Lead [CLP] | Low | ILM05.4 | 250 grams | (1) 8 oz. glass jar w/Teflon lined cap | Cool to 4°C | 180 days |
| Aqueous** | 12 | Total Lead [CLP] | Low | ILM05.4 | 1 liter | (1) 1-liter. Polyethylene bottle w/Teflon lined cap | $HNO_3$ to pH<2, Cool to 4°C | 180 days |
| Rinsate*** | 8 | Total Lead [CLP] | Low | ILM05.4 | 250 mL | (1) 1-liter. Polyethylene bottle w/Teflon lined cap | $HNO_3$ to pH<2; cool to 4°C | 180 days |
| Particulate | 50 | Total Lead | Low | NIOSH Method 7082 | 1 filter | 0.8-micron cellulose ester membrane | none | 180 days |

*Includes soil and sediment samples, and their duplicates.
** Includes groundwater, surface water, and their duplicates.
*** One equipment rinsate blank sample will be collected per day.
$HNO_3$ = Nitric acid.
mL = milliliters.
°C = Degrees Centigrade.

## QAPP Worksheet #20: Field Quality Control Sample Summary Table

| Matrix | Analytical Group | Concentration Level | Analytical and Preparation SOP Reference | No. of Sampling Locations | No. of Field Duplicate Pairs | No. of Extra Volume Laboratory QC (e.g., MS/MSD) Samples | No. of Rinsate Blanks*** | No. of Trip. Blanks | No of PE Samples | Total No. of Samples to Lab |
|---|---|---|---|---|---|---|---|---|---|---|
| Soil* | Lead (FPXRF) | Low | SOM01.2 | 204 | 1/20 samples per matrix | NR | NR | NR | NR | 214 |
| | Total Lead | Low | ILM05.4 | 20 | | 1/20 samples per matrix | 2-6 | NR | NR | 23-27 |
| | TCLP Lead | Low | SOM01.2 | 20 | | 1/20 samples per matrix | NR | NR | NR | 21 |
| | SPLP Lead | Low | SOM01.2 | 20 | | 1/20 samples per matrix | NR | NR | NR | 21 |
| Aqueous** | Total Lead | Low | ILM05.4 | 5 +5 | | 1/20 samples per matrix | 1 | NR | NR | 11 |

*Includes soil and sediment samples, and their duplicates.
** Includes groundwater, surface water, and their duplicates.
*** One equipment rinsate blank sample will be collected per day.
MS/MSD – Matrix Spike/Matrix Spike Duplicate
NR – not required

## QAPP Worksheet #21: Project Sampling SOP References Table

| Reference Number | Title, Revision Date and/or Number | Originating Organization | Equipment Type | Modified for Project Work? (Y/N) | Comments |
|---|---|---|---|---|---|
| SOP #2001 | General Field Sampling Guidelines | EPA/OSWER/ERT | Plastic scoops | N | |
| SOP # 2012 | Soil Sampling from the Compendium of ERT Soil Sampling and Surface Geophysics Procedures. | EPA/OSWER/ERT | Plastic scoops | N | |
| SOP # 2016 | Sediment Sampling from the Compendium of ERT Soil Sampling and Surface Geophysics Procedures. | EPA/OSWER/ERT | Plastic scoops | N | |
| SOP # 2007 | Groundwater Sampling from the Compendium of ERT Soil Sampling and Surface Geophysics Procedures. | EPA/OSWER/ERT | Peristaltic Pump, Tubing, Water Quality Meter | N | |
| SOP # 2013 | Surface Water Sampling from the Compendium of ERT Soil Sampling and Surface Geophysics Procedures. | EPA/OSWER/ERT | Water Quality Meter | N | |
| SOP# 2006 | Sampling Equipment Decontamination (all media); Rev 0.0 August 1994 | EPA/OSWER/ERT | Non-phosphate Detergent, Tap Water. Distilled/Deionized Water, 10% Nitric Acid, Solvent Rinse (Pesticide Grade) | N | |
| | EPA Method 6200 Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment | EPA/OSWER/ERT | FPXRF | Y | Drying and sieving not anticipated |
| PN 101475 | Innov-X Model X-50 Field Portable X-ray Fluorescence Unit User's Manual | Innov-X | FPXRF | N | |

See Attachment B for SOP # 2006 and 2012
Note: The website for EPA-ERT SOPs is: www.ert.org/mainContent.asp?section=Products&subsection=List

## QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection Table

| Field Equipment | Calibration Activity | Maintenance Activity | Testing/ Inspection Activity | Frequency | Acceptance Criteria | Corrective Action | Responsible Person | SOP Reference |
|---|---|---|---|---|---|---|---|---|
| MiniRAM Dust Monitor | Calibrate with background air | Check/ replace battery | None | Prior to day's activities | None | Replace battery or Replace Unit | Equipment Vendor | |
| Innov-X Model X-50 FPXRF Unit | Standardize per manufacturer's instructions | None | Periodic standardization | Per manufacturer's instructions | < 20% relative percent difference | Replace Unit | Innov-X | PN 101475 |
| Trimble® GeoXT™ handheld | None | Check/ replace battery | None | Prior to day's activities | None | Replace Unit | GPS Operator | |

## QAPP Worksheet #23

## Analytical SOP References Table

| Reference Number | Title, Revision Date, and/or Number | Definitive or Screening Data | Analytical Group | Instrument | Organization Performing Analysis | Modified for Project Work? (Y/N) |
|---|---|---|---|---|---|---|
| SW-846 | EPA Method 6200 Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment | Screening | Lead | FPXRF | RST 2/Site Project Manager | Y |
| ILM05.4 | USEPA Contract Laboratory Program Statement of Work for Multi-Media, Multi-Concentration Inorganic Analysis,; December 2006 | Definitive | Target Analyte List Lead | ICP-AES / ICP-MS | DESA Laboratory | N |
| ILM05.4 | USEPA Contract Laboratory Program Statement of Work for Multi-Media, Multi-Concentration Inórganic Analysis,; December 2006 | Definitive | TCLP Lead | ICP-AES / ICP-MS | DESA Laboratory | N |
| ILM05.4 | USEPA Contract Laboratory Program Statement of Work for Multi-Media, Multi-Concentration Inorganic Analysis,; December 2006 | Definitive | SPLP Lead | ICP-AES / ICP-MS | DESA Laboratory | N |
| | NIOSH Laboratory Method, Issue 2: August 1994 | Definitive | Lead | Flame AAS | EMSL Analytical | N |

## QAPP Worksheet #24: Analytical Instrument Calibration Table

| Instrument | Calibration Procedure | Frequency of Calibration | Acceptance Criteria | Corrective Action (CA) | Person Responsible for CA | SOP Reference |
|---|---|---|---|---|---|---|
| FPXRF | Factory calibrated | Prior to issuance | Initial calibration/ Continuing calibration: relative percent difference less than or equal to minimum acceptable 20%. | Replace unit. | Innov-X | PN 101475 |
| ICP-AES / ICP-MS | See ILM05.4; as per instrument manufacturer's recommended procedures | ICP-AES or ICP-MS Initial calibration: daily or once every 24 hours and each time the instrument is set up. ICP-AES or ICP-MS Continuing calibration: beginning and end of run and frequency of 10% or every 2 hours during an analysis run. | ICP-AES: As per instrument manufacturer's recommended procedures, with at least 2 standards. ICP-MS: As per instrument manufacturer's recommended procedures, with at least 2 standards. A minimum of three replicate integrations are required for data acquisition. | ICP-AES or ICP-MS: inspect the system, correct problem, re-calibrate, and re-analyze samples. | EPA DESA Laboratory ICP-AES / ICP-MS Technician | ILM05.4 |

## QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

| Instrument/ Equipment | Maintenance Activity | Testing/ Inspection Activity | Frequency | Acceptance Criteria | Corrective Action | Responsible Person | SOP Reference |
|---|---|---|---|---|---|---|---|
| FPXRF | None | Periodic standardization per instrument manufacturer's recommendations | Per instrument manufacturer's recommendations | Relative percent difference less than or equal to minimum acceptable 20%. | Replace unit. | Innov-X, FPXRF Operator | PN 101475 |
| ICP-AES / ICP-MS | As per instrument manufacturer's recommendations | As per instrument manufacturer's recommendations; check connections | As per instrument manufacturer's recommendations | Acceptable re-calibration; see ILM05.4 | Inspect the system, correct problem, re-calibrate and/or reanalyze samples. | EPA DESA Laboratory ICP-AES/ICP-MS Technician | ILM05.4 |

## QAPP Worksheet #26: Sample Handling System

| SAMPLE COLLECTION, PACKAGING, AND SHIPMENT |
|---|
| **Sample Collection (Personnel/Organization):** RST 2 Site Project Manager, Weston Solutions, Inc., Region 2 |
| **Sample Packaging (Personnel/Organization):** RST 2 Site Project Manager and sampling team members, Weston Solutions, Inc., Region 2 |
| **Coordination of Shipment (Personnel/Organization):** RST 2 Site Project Manager, sampling team members, Weston Solutions, Inc., Region 2 |
| **Type of Shipment/Carrier:** FedEx delivery. |
| **SAMPLE RECEIPT AND ANALYSIS** |
| **Sample Receipt (Personnel/Organization):** DESA Laboratory |

| |
|---|
| **Sample Custody and Storage (Personnel/Organization):** EPA DESA Laboratory |
| **Sample Preparation (Personnel/Organization):** EPA DESA Laboratory |
| **Sample Determinative Analysis (Personnel/Organization):** EPA DESA Laboratory |
| **SAMPLE ARCHIVING** |
| **Field Sample Storage (No. of days from sample collection):** Up to 60 days |
| **Sample Extract/Digestate Storage (No. of days from extraction/digestion):** up to 60 days |
| **Biological Sample Storage (No. of days from sample collection):** N/A |
| **SAMPLE DISPOSAL** |
| **Personnel/Organization:** Sample Technicians, EPA DESA Laboratory |
| **Number of Days from Analysis:** Until analysis and QA/QC checks are completed; as per analytical methodology; see Worksheet #19. |

## QAPP Worksheet #27: Sample Custody Requirements

**Sample Identification Procedures:** Each sample collected by Region II RST 2 will be designated by a code that will identify the sample matrix. The sample location and sample depth will follow the matrix. A hyphen will separate the matrix, sample location, and sample depth. This will then be followed by the sample number. Samples will also be labeled with a CLP assigned number. Specific media types are as follows:

S – Soil; SD – Sediment; GW – Groundwater; SW – Surface Water; RB – Rinsate Blank

Matrix - Sample Location – Depth (e.g. S–A5–0102)

Duplicate samples will be identified in the same manner as other samples and will be distinguished with an –E suffix and documented in the field logbook.

**Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):** Each sample will be individually identified and labeled after collection, then sealed with custody seals. Each sample bottle will be sealed and labeled according to the following protocol. The cap will be secured with custody seals. The bottle label will contain all required information including site/project code and sample number, time and date of collection, analyses requested, and preservative used. The sealed bottle will be placed in plastic coolers, and padded with an absorbent material such as vermiculite. All packaging will conform to IATA shipping regulations for overnight carriers.

The sample information will be recorded on chain-of custody (COC) forms, and the samples shipped to the appropriate laboratory via overnight delivery service or courier. The sample documents will be sealed in a plastic bag and affixed to the underside of each cooler lid. The lid will be sealed and affixed on at least two sides with custody seals so that any sign of tampering is easily visible. Chain-of-custody records will be prepared in FORMS II Lite to accompany samples from the time of collection and throughout the shipping process. Each individual in possession of the samples must sign and date the sample COC Record. The chain-of-custody record will be considered completed upon receipt at the laboratory. A traffic report and chain-of-custody record will be maintained from the time the sample is taken to its final deposition. Every transfer of custody must be noted and signed for, and a copy of this record kept by each individual who has signed. When samples are not under direct control of the individual responsible for them, they must be stored in a locked container sealed with a custody seal. Specific information regarding custody of the samples projected to be collected on the weekend will be noted in the field logbook. The COC record should include (at minimum) the following: 1) Sample identification number; 2) Sample information; 3) Sample location; 4) Sample date; 5) Sample Time; 6) Sample Type Matrix; 7) Sample Container Type; 8) Sample Analysis Requested; 9) Name(s) and signature(s) of sampler(s); and 10) Signature(s) of any individual(s) with custody of samples.

A separate COC form must accompany each cooler for each daily shipment. The chain-of-custody form must address all samples in that cooler, but not address samples in any other cooler. This practice maintains the COC for all samples in case of mis-shipment.

## QAPP Worksheet #27: Sample Custody Requirements (concluded)

**Laboratory Sample Custody Procedures (receipt of samples, archiving, and disposal):** Within the laboratory, the person responsible for sample receipt must sign and date the COC form; examine all samples for possible shipping damage and improper sample preservation; note on the COC record that specific samples were damaged; notify sampling personnel as soon as possible so that appropriate samples may be regenerated; verify that sample holding times have not been exceeded; maintain laboratory COC documentation; and place the samples in the appropriate laboratory storage. At this time, no samples will be archived at the laboratory. Disposal of the samples will occur only after analyses and QA/QC checks are completed.

Note: Refer to Contract Laboratory Program Guidance for Field Samplers, EPA-540-R-07-06, July 2007 at:
http://www.epa.gov/superfund/programs/clp/download/sampler/clp_sampler_guidance.pdf

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28A: Field Screen Lead/RST 2 – EPA Method 6200

**(UFP-QAPP Manual Section 3.4)**
Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Soil |
| **Analytical Group** | Field Portable X-Ray Fluorescence Screening (Lead) |
| **Concentration Level** | Low/Medium (mg/kg) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2012 |
| **Analytical Method/SOP Reference** | EPA Method 6200 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | RST 2 |
| **No. of Sample Locations** | 20 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| $SiO_2$ Blank | Beginning and end of each day | No constituent > CRQL | Suspend analysis until source rectified | FPXRF Operator | Accuracy | No constituent > CRQL |
| Field Duplicate | 1 per ≤ 20 samples | ± 20% RPD** | Flag outliers | FPXRF Operator | Precision | ± 20% RPD** |
| Standardization check | Per manufacturer's recommendation | Pass/fail | Replace unit | FPXRF Operator | Accuracy | 75-125%R |
| Laboratory duplicate | 1 per ≤ 20 samples | ± 20% RPD** | Flag outliers | FPXRF Operator | Precision | ± 20% RPD** |

*except when the sample concentration is greater than 4 times the spike concentration, then disregard the recoveries; no data validation action taken
**Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria)
**except when the sample and/or duplicate concentration is less than 5 times the CRQL, then ± CRQL.

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28B: TAL Metals – Inorganics/CLP ILMO5.4

**(UFP-QAPP Manual Section 3.4)**
Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Aqueous |
| **Analytical Group** | Target Analyte List Inorganics Metals (Lead) |
| **Concentration Level** | Low/Medium (µg/L) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2007, 2013 |
| **Analytical Method/SOP Reference** | ILM05.4 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | EPA DESA Laboratory |
| **No. of Sample Locations** | 10 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Preparation Blank | 1 per ≤ 20 samples | No constituent > CRQL | Suspend analysis until source rectified; redigest and reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | No constituent > CRQL |
| Spike | 1 per ≤ 20 samples | 75-125%R* | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R* |
| Duplicate | 1 per ≤ 20 samples | ± 20% RPD** | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Precision | ± 20% RPD** |
| Post-Digestion Spike | after any analyte (except Ag and Hg) fails spike %R | 75-125%R | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R |
| Interference Check Sample [ICP Analysis Only] | beginning, end and periodically (not less than once per 20 samples) | ± 2 times CRQL of true value or ± 20% of true value, whichever is greater | Check calculations and instruments, reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Sensitivity | ± 2 times CRQL of true value or ± 20% of true value, whichever is greater |

*except when the sample concentration is greater than 4 times the spike concentration, then disregard the recoveries; no data validation action taken
**Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria)
**except when the sample and/or duplicate concentration is less than 5 times the CRQL, then ± CRQL.

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28B: TAL Metals – Inorganics/CLP ILMO5.4 [cont'd]

**(UFP-QAPP Manual Section 3.4)**
Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Aqueous |
| **Analytical Group** | Target Analyte List Inorganics Metals (Lead) [cont'd] |
| **Concentration Level** | Low/Medium (µg/L) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2007, 2013 |
| **Analytical Method/SOP Reference** | ILM05.4 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | EPA DESA Laboratory |
| **No. of Sample Locations** | Up to 9 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Laboratory Control Sample | 1 per ≤ 20 samples | 80-120%R (except Ag and Sb) | Suspend analysis until source rectified; redigest and reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 80-120%R (except Ag and Sb) |

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28C: TAL Metals – Inorganics/CLP ILMO5.4

**(UFP-QAPP Manual Section 3.4)**

Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Soil |
| **Analytical Group** | Target Analyte List Inorganics Metals (Lead) |
| **Concentration Level** | Low/Medium (mg/kg) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2012, 2016 |
| **Analytical Method/SOP Reference** | ILM05.4 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | EPA DESA Laboratory |
| **No. of Sample Locations** | 20 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Preparation Blank | 1 per ≤ 20 samples | No constituent > CRQL | Suspend analysis until source rectified; redigest and reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | No constituent > CRQL |
| Spike | 1 per ≤ 20 samples | 75-125%R* | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R* |
| Duplicate | 1 per ≤ 20 samples | ± 20% RPD** | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Precision | ± 20% RPD** |
| Post-Digestion Spike | after any analyte (except Ag and Hg) fails spike %R | 75-125%R | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R |
| Interference Check Sample [ICP Analysis Only] | beginning, end and periodically during run (2 times every 8 hours) | Within ± 2 times CRQL of true value or ± 20% of true value, whichever is greater | Check calculations and instruments, reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Sensitivity | Within ± 2 times CRQL of true value or ± 20% of true value, whichever is greater |

*except when the sample concentration is greater than 4 times the spike concentration, then disregard the recoveries; no data validation action taken
**Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria)
**except when the sample and/or duplicate concentration is less than 5 times the CRQL, then ± CRQL.

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28C: TAL Metals – Inorganics/CLP ILMO5.4 [cont'd]

**(UFP-QAPP Manual Section 3.4)**
Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Soil |
| **Analytical Group** | Target Analyte List Inorganics Metals (Lead) [cont'd] |
| **Concentration Level** | Low/Medium (mg/kg) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2012, 2016 |
| **Analytical Method/SOP Reference** | ILM05.4 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | EPA DESA Laboratory |
| **No. of Sample Locations** | 20 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Laboratory Control Sample | 1 per ≤ 20 samples | Control limits established by EPA* | Suspend analysis until source rectified; redigest and reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | Control limits established by EPA* |

* If the EPA LCS is unavailable, other EPA QC samples or other certified materials may be used. In such cases, control limits for the LCS must be documented and provided.

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28D: TAL Metals – Inorganics/CLP ILMO5.4

**(UFP-QAPP Manual Section 3.4)**

Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Soil |
| **Analytical Group** | Toxicity Characteristic Leaching Procedure (Lead) |
| **Concentration Level** | Low/Medium (µg/L) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2012 |
| **Analytical Method/SOP Reference** | 1311 Extraction/ILM05.4 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | EPA DESA Laboratory |
| **No. of Sample Locations** | 20 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Preparation Blank | 1 per ≤ 20 samples | No constituent > CRQL | Suspend analysis until source rectified; redigest and reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | No constituent > CRQL |
| Spike | 1 per ≤ 20 samples | 75-125%R* | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R* |
| Duplicate | 1 per ≤ 20 samples | ± 20% RPD** | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Precision | ± 20% RPD** |
| Post-Digestion Spike | after any analyte (except Ag and Hg) fails spike %R | 75-125%R | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R |
| Interference Check Sample [ICP Analysis Only] | beginning, end and periodically during run (2 times every 8 hours) | Within ± 2 times CRQL of true value or ± 20% of true value, whichever is greater | Check calculations and instruments, reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Sensitivity | Within ± 2 times CRQL of true value or ± 20% of true value, whichever is greater |

*except when the sample concentration is greater than 4 times the spike concentration, then disregard the recoveries; no data validation action taken
**Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria)
**except when the sample and/or duplicate concentration is less than 5 times the CRQL, then ± CRQL.

## QAPP Worksheet #28: QC Samples Table
## Worksheet # 28E: TAL Metals – Inorganics/CLP ILMO5.4

**(UFP-QAPP Manual Section 3.4)**
Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limit exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

| | |
|---|---|
| **Matrix** | Soil |
| **Analytical Group** | Synthetic Precipitation Leaching Procedure (Lead) |
| **Concentration Level** | Low/Medium (µg/L) |
| **Sampling SOP(s)** | EPA ERT SOP No. 2012 |
| **Analytical Method/SOP Reference** | 1312 Extraction/ILM05.4 |
| **Sampler's Name** | Joseph Schmidl, PG, CWS |
| **Field Sampling Organization** | Weston Solutions, Inc. |
| **Analytical Organization** | EPA DESA Laboratory |
| **No. of Sample Locations** | 20 |

| Lab QC Sample: | Frequency/Number | Method/SOP QC Acceptance Limits | Corrective Action | Person(s) Responsible for Corrective Action | Data Quality Indicator (DQI) | Measurement Performance Criteria |
|---|---|---|---|---|---|---|
| Preparation Blank | 1 per ≤ 20 samples | No constituent > CRQL | Suspend analysis until source rectified; redigest and reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | No constituent > CRQL |
| Spike | 1 per ≤ 20 samples | 75-125%R* | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R* |
| Duplicate | 1 per ≤ 20 samples | ± 20% RPD** | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Precision | ± 20% RPD** |
| Post-Digestion Spike | after any analyte (except Ag and Hg) fails spike %R | 75-125%R | Flag outliers | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Accuracy | 75-125%R |
| Interference Check Sample [ICP Analysis Only] | beginning, end and periodically during run (2 times every 8 hours) | Within ± 2 times CRQL of true value or ± 20% of true value, whichever is greater | Check calculations and instruments, reanalyze affected samples | EPA DESA Laboratory ICP-AES/ICP-MS Technician | Sensitivity | Within ± 2 times CRQL of true value or ± 20% of true value, whichever is greater |

*except when the sample concentration is greater than 4 times the spike concentration, then disregard the recoveries; no data validation action taken
**Reference USEPA Region 2 SOP No. HW-2, Revision 13/Evaluation of Metals Data for CLP - (include absolute difference criteria)
**except when the sample and/or duplicate concentration is less than 5 times the CRQL, then ± CRQL.

## QAPP Worksheet #29: Project Documents and Records Table

| Sample Collection Documents and Records | Analysis Documents and Records | Data Assessment Documents and Records | Other |
|---|---|---|---|
| • Site and field logbooks<br>• COC forms<br>• Field Data Sheets<br>• GIS map for sampling locations | • Sample receipt logs<br>• Internal and external COC forms<br>• Equipment calibration logs<br>• Sample preparation worksheets/logs<br>• Sample analysis worksheets/run logs<br>• Telephone/email logs<br>• Corrective action documentation | • Data validation reports<br>• Field inspection checklist(s)<br>• Laboratory Audit checklist (if performed)<br>• Review forms for electronic entry of data into database<br>• Corrective action documentation<br>• Laboratory Final Data | CLP request form<br>Health and Safety Plan |

## QAPP Worksheet #30: Analytical Services Table

| Matrix | Analytical Group | Concentration Level | Analytical SOP | Laboratory Data Package Turnaround Time | Laboratory/Organization (Name and Address, Contact Person and Telephone Number) | Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number) |
|---|---|---|---|---|---|---|
| Soil | Lead | Low | EPA Method 6200 | 1 day, electronic | RST 2, Site Project Manager, FPXRF Unit – Field Screening Analysis | NA |
| Aqueous and Soil | Total Lead | Low | ILM05.4 | 3 weeks written | EPA DESA Laboratory | NA |

| Matrix | Analytical Group | Concentration Level | Analytical SOP | Laboratory Data Package Turnaround Time | Laboratory/Organization (Name and Address, Contact Person and Telephone Number) | Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number) |
|---|---|---|---|---|---|---|
| Soil | TCLP Lead | Low | ILM05.4 | 3 weeks written | EPA DESA Laboratory | NA |
| | SPLP Lead | Low | ILM05.4 | 3 weeks written | EPA DESA Laboratory | NA |

## QAPP Worksheet #31

## Planned Project Assessments Table

| Assessment Type | Frequency | Internal or External | Organization Performing Assessment | Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation) | Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation) | Person(s) Responsible for Identifying and Implementing Corrective Actions (Title and Organizational Affiliation) | Person(s) Responsible for Monitoring Effectiveness of Corrective Actions (Title and Organizational Affiliation) |
|---|---|---|---|---|---|---|---|
| Laboratory Technical Systems | Every Year | External | Regulatory Agency | Regulatory Agency | EPA DESA Laboratory | EPA DESA Laboratory | EPA or other Regulatory Agency |
| Performance Evaluation Samples** | None requested | External | Regulatory Agency | Regulatory Agency | EPA DESA Laboratory | EPA DESA Laboratory | EPA or other Regulatory Agency |
| Peer Review | Each Deliverable | Internal | Weston Solutions, Inc. | QAO, Group Leader, and Readiness Coordinator | SPM, Weston Solutions, Inc. | SPM, Weston Solutions, Inc. | EPA OSC and/or EPA QAO |

## QAPP Worksheet #32

## Assessment Findings and Corrective Action Responses

| Assessment Type | Nature of Deficiencies Documentation | Individual(s) Notified of Findings (Name, Title, Organization) | Timeframe of Notification | Nature of Corrective Action Response Documentation | Individual(s) Receiving Corrective Action Response (Name, Title, Org.) | Timeframe for Response |
|---|---|---|---|---|---|---|
| Project Readiness Review | Checklist or logbook entry summary | Site Project Manager, Weston Solutions, Inc. | Immediately to within 24 hours of review | Checklist or logbook entry | Site Project Manager, Weston Solutions, Inc. | Immediately to within 24 hours of review |
| Field Observations/ Deviations from Work Plan | Logbook | Site Project Manager, Weston Solutions, Inc. and EPA RPM | Immediately to within 24 hours of deviation | Logbook | Site Project Manager, Weston Solutions, Inc.and EPA RPM | Immediately to within 24 hours of deviation |
| Laboratory Technical Systems/ Performance Audits | Written Report | EPA CLP Laboratory | 30 days | Letter | EPA CLP Laboratory | 14 days |
| On-Site Field Inspection | Written Report | Site Project Manager, Weston Solutions, Inc. | 7 calendar days after completion of the audit | Letter/Internal Memorandum | Site Project Manager, Weston Solutions, Inc. and/or EPA RPM | To be identified in the cover letter of the report |
| Peer Review | Deliverables | SPM, Weston Solutions, Inc. | Prior to deliverable due date | Comments directly on deliverable | SPM, Weston Solutions, Inc. | Prior to deliverable due date |

## QAPP Worksheet #33
## QA Management Reports Table

| Type of Report | Frequency (daily, weekly, monthly, quarterly, annually, etc.) | Projected Delivery Date(s) | Person(s) Responsible for Report Preparation (Title and Organizational Affiliation) | Report Recipient(s) (Title and Organizational Affiliation) |
|---|---|---|---|---|
| EPA DESA Laboratory Data (unvalidated) | As performed | Unknown | EPA DESA Laboratory | Adly Michael, RSCC, EPA Region 2 and Site Project Manager, Weston Solutions, Inc. |
| EPA DESA Laboratory Data (validated) | As performed | Up to 60 days after receipt of unvalidated data | EPA Region 2 | Site Project Manager, Weston Solutions, Inc. |
| Laboratory Technical Systems/ Performance Audits | As performed | Unknown | EPA or other Regulatory Agency | EPA DESA Laboratory |
| Performance Evaluation Samples | Not requested | Unknown | EPA or other Regulatory Agency | EPA DESA Laboratory |
| On-Site Field Inspection | As performed | 7 calendar days after completion of the inspection | Site Project Manager, Weston Solutions, Inc. | Site Project Manager, Weston Solutions, Inc. |
| Field Change Request | As required per field change | Three days after identification of need for field change | Site Project Manager, Weston Solutions, Inc. | EPA OSC |
| Final Report | As performed | 2 weeks after receipt of EPA approval of data package | Site Project Manager, Weston Solutions, Inc. | EPA OSC |

## QAPP Worksheet #34
## Verification (Step I) Process Table

| Verification Input | Description | Internal/ External | [1]Responsible for Verification (Name, Organization) |
|---|---|---|---|
| Site/field logbooks | Field notes will be prepared daily by the RST 2 Site Project Manager and will be complete, appropriate, legible and pertinent. Upon completion of field work, logbooks will be placed in the project files. | I | Site Project Manager, Weston Solutions, Inc. |
| Chains of Custody | COC forms will be reviewed against the samples packed in the specific cooler prior to shipment. The reviewer will initial the form. An original COC will be sent with the samples to the laboratory, while copies are retained for (1) the Sampling Trip Report and (2) the project files. | I | Site Project Manager, Weston Solutions, Inc. |
| Sampling Trip Reports | STRs will be prepared for each week of field sampling [for which samples are sent to an EPA DESA laboratory.] Information in the STR will be reviewed against the COC forms, and potential discrepancies will be discussed with field personnel to verify locations, dates, etc. | I | Site Project Manager, Weston Solutions, Inc. |
| Laboratory Preliminary Data | Preliminary data – limited review for either contract compliance or technical compliance. | E | EPA DESA Laboratory |
| Laboratory analytical data package | Data packages will be reviewed/verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal. | E | EPA DESA Laboratory |
| Laboratory analytical data package | Data packages will be reviewed as to content and sample information upon receipt by EPA. | I/E | ESAT Data Validation Personnel, EPA Region 2 |
| Final Sample Report | The project data results will be compiled in a sample report for the project. Entries will be reviewed/verified against hardcopy information. | I | Site Project Manager, Weston Solutions, Inc. |

[1] Responsible for verifications, and their name and organization will be added

## QAPP Worksheet #35
## Validation (Steps IIa and IIb) Process Table

| Step IIa/IIb | Validation Input | Description | Responsible for Validation (Name, Organization) |
|---|---|---|---|
| IIa | SOPs | Ensure that the sampling methods/procedures outlined in QAPP were followed, and that any deviations were noted/approved. | Site Project Manager, Weston Solutions, Inc. |
| IIb | SOPs | Determine potential impacts from noted/approved deviations, in regard to PQOs. | Site Project Manager, Weston Solutions, Inc. |
| IIa | Chains of custody | Examine COC forms against QAPP and laboratory contract requirements (e.g., analytical methods, sample identification, etc.). | ESAT Data Validation Personnel, EPA Region 2 |
| IIa | Laboratory data package | Examine packages against QAPP and laboratory contract requirements, and against COC forms (e.g., holding times, sample handling, analytical methods, sample identification, data qualifiers, QC samples, etc.). | ESAT Data Validation Personnel, EPA Region 2, and Site Project Manager, Weston Solutions, Inc. |
| IIb | Laboratory data package | Determine potential impacts from noted/approved deviations, in regard to PQOs. Examples include Practical Quantitation Limits and QC sample limits (precision/accuracy). | ESAT Data Validation Personnel, EPA Region 2, and Site Project Manager, Weston Solutions, Inc. |
| IIb | Field duplicates* | Compare results of field duplicate (or replicate) analyses with RPD criteria | ESAT Data Validation Personnel, EPA Region 2, and Site Project Manager, Weston Solutions, Inc. |

* Site-specific QAPP may contain additional data validation inputs as required by the project objectives.

## QAPP Worksheet #36: Validation (Steps IIa and IIb) Summary Table

| Step IIa/IIb | Matrix | Analytical Group | Concentration Level | Validation Criteria | Data Validator (title and organizational affiliation) |
|---|---|---|---|---|---|
| IIa/IIb | Soil/ Aqueous | Total Lead | Low and Medium | Data Validation SOP for Inorganic Analysis of Low/Medium Concentrations Metals under SOW ILM05.4 | EPA Region 2 Personnel with contractor support |

## QAPP Worksheet #37: Usability Assessment

**Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used:** Data, whether generated in the field or by the laboratory, are tabulated and reviewed for Precision, Accuracy, Representativeness, Completeness, and Comparability (PARCCS) by the SPM for field data or the data validator for laboratory data. The review of the PARCC Data Quality Indicators (DQI) will compare with the DQO detailed in the site-specific QAPP, the analytical methods used and impact of any qualitative and quantitative trends will be examined to determine if bias exists. A hard copy of field data is maintained in a designated field or site logbook. Laboratory data packages are validated, and final data reports are generated. All documents and logbooks are assigned unique and specific control numbers to allow tracking and management.

Where applicable, the following documents will be followed to evaluate data for fitness in decision making: EPA QA/G-4, *Guidance on Systematic Planning using the Data Quality Objectives Process*, EPA/240/B-06/001, February 2006, and EPA QA/G-9R, *Guidance for Data Quality Assessment*, A reviewer's Guide EPA/240/B-06/002, February 2006.

**Describe the evaluative procedures used to assess overall measurement error associated with the project:**

As delineated in the ***Uniform Federal Policy for Implementing Environmental Quality Systems: Evaluating, Assessing and Documenting Environmental Data Collection and Use Programs Part 1: UFP-QAPP (EPA-505-B-04-900A, March 2005); Part 2A: UFP-QAPP Workbook (EPA-505-B-04-900C, March 2005); Part 2B: Quality Assurance/Quality Control Compendium: Non-Time Critical QA/QC Activities (EPA-505-B-04-900B, March 2005);*** "Graded Approach" will be implemented for data collection activities that are either exploratory or small in nature or where specific decisions cannot be identified, since this guidance indicates that the formal DQO process is not necessary.

The data will be evaluated to determine whether they satisfy the PQO for the project, as outlined in QAPP Worksheet #15. The validation process determines if the data satisfy the QA criteria. After the data pass the data validation process, comparison of results with the PQO is done. For example, at the Jewett White Lead Company Site, QAPP Worksheet #15 specifies that the soil data are to be compared to New York Department of Environmental Conservation Restricted Use Soil Cleanup Objectives for this investigation; therefore, the results can then be used to determine if additional sampling is necessary to determine the extent of contamination.

**Identify the personnel responsible for performing the usability assessment:** Site Project Management Team, Data Validation Personnel, and EPA Region 2 OSC.

**Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:** A copy of the most current approved QAPP, including any graphs, maps and text reports developed will be provided to all personnel identified on the distribution list.

and

# Attachment A
# Sample Location Map

# Attachment B
# Standard Operating Procedures

# GENERAL FIELD SAMPLING GUIDELINES

SOP#: 2001
DATE: 08/11/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to provide general field sampling guidelines that will assist REAC personnel in choosing sampling strategies, location, and frequency for proper assessment of site characteristics. This SOP is applicable to all field activities that involve sampling.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Sampling is the selection of a representative portion of a larger population, universe, or body. Through examination of a sample, the characteristics of the larger body from which the sample was drawn can be inferred. In this manner, sampling can be a valuable tool for determining the presence, type, and extent of contamination by hazardous substances in the environment.

The primary objective of all sampling activities is to characterize a hazardous waste site accurately so that its impact on human health and the environment can be properly evaluated. It is only through sampling and analysis that site hazards can be measured and the job of cleanup and restoration can be accomplished effectively with minimal risk. The sampling itself must be conducted so that every sample collected retains its original physical form and chemical composition. In this way, sample integrity is insured, quality assurance standards are maintained, and the sample can accurately represent the larger body of material under investigation.

The extent to which valid inferences can be drawn from a sample depends on the degree to which the sampling effort conforms to the project's objectives. For example, as few as one sample may produce adequate, technically valid data to address the project's objectives. Meeting the project's objectives requires thorough planning of sampling activities, and implementation of the most appropriate sampling and analytical procedures. These issues will be discussed in this procedure.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample to be collected, and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest. Sample preservation, containers, handling, and storage for air and waste samples are discussed in the specific SOPs for air and waste sampling techniques.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

The nature of the object or materials being sampled may be a potential problem to the sampler. If a material is homogeneous, it will generally have a uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the sampler because of changes in the material over distance, both laterally and vertically.

Samples of hazardous materials may pose a safety threat to both field and laboratory personnel. Proper health and safety precautions should be implemented when handling this type of sample.

Environmental conditions, weather conditions, or non-target chemicals may cause problems and/or interferences when performing sampling activities or when sampling for a specific parameter. Refer to the specific SOPs for sampling techniques.

## 5.0 EQUIPMENT/APPARATUS

The equipment/apparatus required to collect samples must be determined on a site specific basis. Due to the wide variety of sampling equipment available, refer to the specific SOPs for sampling techniques which include lists of the equipment/apparatus required for sampling.

## 6.0 REAGENTS

Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

## 7.0 PROCEDURE

### 7.1 Types of Samples

In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample.

Environmental samples are those collected from streams, ponds, lakes, wells, and are off-site samples that are not expected to be contaminated with hazardous materials. They usually do not require the special handling procedures typically used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples.

Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, or areas previously identified as contaminated, and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling and shipping any wastes believed to be concentrated regardless of the degree.

The importance of making the distinction between environmental and hazardous samples is two-fold:

(1) Personnel safety requirements: Any sample thought to contain enough hazardous materials to pose a safety threat should be designated as hazardous and handled in a manner which ensures the safety of both field and laboratory personnel.

(2) Transportation requirements: Hazardous samples must be packaged, labeled, and shipped according to the International Air Transport Association (IATA) Dangerous Goods Regulations or Department of Transportation (DOT) regulations and U.S. EPA guidelines.

### 7.2 Sample Collection Techniques

In general, two basic types of sample collection techniques are recognized, both of which can be used for either environmental or hazardous samples.

Grab Samples

A grab sample is defined as a discrete aliquot representative of a specific location at a given point in time. The sample is collected all at once at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials being sampled. In general, as sources vary over time and distance, the representativeness of grab samples will decrease.

Composite Samples

Composites are nondiscrete samples composed of more than one specific aliquot collected at various sampling locations and/or different points in time. Analysis of this type of sample produces an average value and can in certain instances be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits.

Compositing is often used for environmental samples and may be used for hazardous samples under certain conditions. For example, compositing of hazardous waste is often performed after compatibility tests have

been completed to determine an average value over a number of different locations (group of drums). This procedure generates data that can be useful by providing an average concentration within a number of units, can serve to keep analytical costs down, and can provide information useful to transporters and waste disposal operations.

For sampling situations involving hazardous wastes, grab sampling techniques are generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing.

## 7.3 Types of Sampling Strategies

The number of samples that should be collected and analyzed depends on the objective of the investigation. There are three basic sampling strategies: random, systematic, and judgmental sampling.

Random sampling involves collection of samples in a nonsystematic fashion from the entire site or a specific portion of a site. Systematic sampling involves collection of samples based on a grid or a pattern which has been previously established. When judgmental sampling is performed, samples are collected only from the portion(s) of the site most likely to be contaminated. Often, a combination of these strategies is the best approach depending on the type of the suspected/known contamination, the uniformity and size of the site, the level/type of information desired, etc.

## 7.4 QA Work Plans (QAWP)

A QAWP is required when it becomes evident that a field investigation is necessary. It should be initiated in conjunction with, or immediately following, notification of the field investigation. This plan should be clear and concise and should detail the following basic components, with regard to sampling activities:

- Objective and purpose of the investigation.
- Basis upon which data will be evaluated.
- Information known about the site including location, type and size of the facility, and length of operations/abandonment.
- Type and volume of contaminated material, contaminants of concern (including concentration), and basis of the information/data.
- Technical approach including media/matrix to be sampled, sampling equipment to be used, sample equipment decontamination (if necessary), sampling design and rationale, and SOPs or description of the procedure to be implemented.
- Project management and reporting, schedule, project organization and responsibilities, manpower and cost projections, and required deliverables.
- QA objectives and protocols including tables summarizing field sampling and QA/QC analysis and objectives.

Note that this list of QAWP components is not all-inclusive and that additional elements may be added or altered depending on the specific requirements of the field investigation. It should also be recognized that although a detailed QAWP is quite important, it may be impractical in some instances. Emergency responses and accidental spills are prime examples of such instances where time might prohibit the development of site-specific QAWPs prior to field activities. In such cases, investigators would have to rely on general guidelines and personal judgment, and the sampling or response plans might simply be a strategy based on preliminary information and finalized on site. In any event, a plan of action should be developed, no matter how concise or informal, to aid investigators in maintaining a logical and consistent order to the implementation of their task.

## 7.5 Legal Implications

The data derived from sampling activities are often introduced as critical evidence during litigation of a hazardous waste site cleanup. Legal issues in which sampling data are important may include cleanup cost recovery, identification of pollution sources and responsible parties, and technical validation of remedial design methodologies. Because of the potential for involvement in legal actions, strict adherence to technical and administrative SOPs is essential during both the development and implementation of sampling activities.

Technically valid sampling begins with thorough planning and continues through the sample collection and analytical procedures. Administrative requirements involve thorough, accurate

documentation of all sampling activities. Documentation requirements include maintenance of a chain of custody, as well as accurate records of field activities and analytical instructions. Failure to observe these procedures fully and consistently may result in data that are questionable, invalid and non-defensible in court, and the consequent loss of enforcement proceedings.

## 8.0 CALCULATIONS

Refer to the specific SOPs for any calculations which are associated with sampling techniques.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

Refer to the specific SOPs for the type and frequency of QA/QC samples to be analyzed, the acceptance criteria for the QA/QC samples, and any other QA/QC activities which are associated with sampling techniques.

## 10.0 DATA VALIDATION

Refer to the specific SOPs for data validation activities that are associated with sampling techniques.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety procedures.

# SAMPLING EQUIPMENT DECONTAMINATION

SOP#: 2006
DATE: 08/11/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to provide a description of the methods used for preventing, minimizing, or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during hazardous waste operations as per 29 Code of Federal Regulations (CFR) 1910.120. This SOP does not address personnel decontamination.

These are standard (i.e. typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitation, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Removing or neutralizing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances.

Gross contamination can be removed by physical decontamination procedures. These abrasive and non-abrasive methods include the use of brushes, air and wet blasting, and high and low pressure water cleaning.

The first step, a soap and water wash, removes all visible particulate matter and residual oils and grease. This may be preceded by a steam or high pressure water wash to facilitate residuals removal. The second step involves a tap water rinse and a distilled/deionized water rinse to remove the detergent. An acid rinse provides a low pH media for trace metals removal and is included in the decontamination process if metal samples are to be collected. It is followed by another distilled/deionized water rinse. If sample analysis does not include metals, the acid rinse step can be omitted. Next, a high purity solvent rinse is performed for trace organics removal if organics are a concern at the site. Typical solvents used for removal of organic contaminants include acetone, hexane, or water. Acetone is typically chosen because it is an excellent solvent, miscible in water, and not a target analyte on the Priority Pollutant List. If acetone is known to be a contaminant of concern at a given site or if Target Compound List analysis (which includes acetone) is to be performed, another solvent may be substituted. The solvent must be allowed to evaporate completely and then a final distilled/deionized water rinse is performed. This rinse removes any residual traces of the solvent.

The decontamination procedure described above may be summarized as follows:

1. Physical removal
2. Non-phosphate detergent wash
3. Tap water rinse
4. Distilled/deionized water rinse
5. 10% nitric acid rinse
6. Distilled/deionized water rinse
7. Solvent rinse (pesticide grade)
8. Air dry
9. Distilled/deionized water rinse

If a particular contaminant fraction is not present at the site, the nine (9) step decontamination procedure specified above may be modified for site specificity. For example, the nitric acid rinse may be eliminated if metals are not of concern at a site. Similarly, the solvent rinse may be eliminated if organics are not of

concern at a site. Modifications to the standard procedure should be documented in the site specific work plan or subsequent report.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample to be collected and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest.

More specifically, sample collection and analysis of decontamination waste may be required before beginning proper disposal of decontamination liquids and solids generated at a site. This should be determined prior to initiation of site activities.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- The use of distilled/deionized water commonly available from commercial vendors may be acceptable for decontamination of sampling equipment provided that it has been verified by laboratory analysis to be analyte free (specifically for the contaminants of concern).
- The use of an untreated potable water supply is not an acceptable substitute for tap water. Tap water may be used from any municipal or industrial water treatment system.
- If acids or solvents are utilized in decontamination they raise health and safety, and waste disposal concerns.
- Damage can be incurred by acid and solvent washing of complex and sophisticated sampling equipment.

## 5.0 EQUIPMENT/APPARATUS

Decontamination equipment, materials, and supplies are generally selected based on availability. Other considerations include the ease of decontaminating or disposing of the equipment. Most equipment and supplies can be easily procured. For example, soft-bristle scrub brushes or long-handled bottle brushes can be used to remove contaminants. Large galvanized wash tubs, stock tanks, or buckets can hold wash and rinse solutions. Children's wading pools can also be used. Large plastic garbage cans or other similar containers lined with plastic bags can help segregate contaminated equipment. Contaminated liquid can be stored temporarily in metal or plastic cans or drums.

The following standard materials and equipment are recommended for decontamination activities:

### 5.1 Decontamination Solutions

- Non-phosphate detergent
- Selected solvents (acetone, hexane, nitric acid, etc.)
- Tap water
- Distilled or deionized water

### 5.2 Decontamination Tools/Supplies

- Long and short handled brushes
- Bottle brushes
- Drop cloth/plastic sheeting
- Paper towels
- Plastic or galvanized tubs or buckets
- Pressurized sprayers ($H_2O$)
- Solvent sprayers
- Aluminum foil

### 5.3 Health and Safety Equipment

Appropriate personal protective equipment (i.e., safety glasses or splash shield, appropriate gloves, aprons or coveralls, respirator, emergency eye wash)

### 5.4 Waste Disposal

- Trash bags
- Trash containers
- 55-gallon drums
- Metal/plastic buckets/containers for storage and disposal of decontamination solutions

## 6.0 REAGENTS

There are no reagents used in this procedure aside from the actual decontamination solutions. Table 1 (Appendix A) lists solvent rinses which may be required for elimination of particular chemicals. In

general, the following solvents are typically utilized for decontamination purposes:

- 10% nitric acid is typically used for inorganic compounds such as metals. An acid rinse may not be required if inorganics are not a contaminant of concern.
- Acetone (pesticide grade)[1]
- Hexane (pesticide grade)[1]
- Methanol[1]

[1] - Only if sample is to be analyzed for organics.

## 7.0 PROCEDURES

As part of the health and safety plan, a decontamination plan should be developed and reviewed. The decontamination line should be set up before any personnel or equipment enter the areas of potential exposure. The equipment decontamination plan should include:

- The number, location, and layout of decontamination stations.
- Decontamination equipment needed.
- Appropriate decontamination methods.
- Methods for disposal of contaminated clothing, equipment, and solutions.
- Procedures can be established to minimize the potential for contamination. This may include: (1) work practices that minimize contact with potential contaminants; (2) using remote sampling techniques; (3) covering monitoring and sampling equipment with plastic, aluminum foil, or other protective material; (4) watering down dusty areas; (5) avoiding laying down equipment in areas of obvious contamination; and (6) use of disposable sampling equipment.

## 7.1 Decontamination Methods

All samples and equipment leaving the contaminated area of a site must be decontaminated to remove any contamination that may have adhered to equipment. Various decontamination methods will remove contaminants by: (1) flushing or other physical action, or (2) chemical complexing to inactivate contaminants by neutralization, chemical reaction, disinfection, or sterilization.

Physical decontamination techniques can be grouped into two categories: abrasive methods and non-abrasive methods, as follows:

### 7.1.1 Abrasive Cleaning Methods

Abrasive cleaning methods work by rubbing and wearing away the top layer of the surface containing the contaminant. The mechanical abrasive cleaning methods are most commonly used at hazardous waste sites. The following abrasive methods are available:

Mechanical

Mechanical methods of decontamination include using metal or nylon brushes. The amount and type of contaminants removed will vary with the hardness of bristles, length of time brushed, degree of brush contact, degree of contamination, nature of the surface being cleaned, and degree of contaminant adherence to the surface.

Air Blasting

Air blasting equipment uses compressed air to force abrasive material through a nozzle at high velocities. The distance between nozzle and surface cleaned, air pressure, time of application, and angle at which the abrasive strikes the surface will dictate cleaning efficiency. Disadvantages of this method are the inability to control the amount of material removed and the large amount of waste generated.

Wet Blasting

Wet blast cleaning involves use of a suspended fine abrasive. The abrasive/water mixture is delivered by compressed air to the contaminated area. By using a very fine abrasive, the amount of materials removed can be carefully controlled.

### 7.1.2 Non-Abrasive Cleaning Methods

Non-abrasive cleaning methods work by forcing the contaminant off a surface with pressure. In general, the equipment surface is not removed using non-abrasive methods.

Low-Pressure Water

This method consists of a container which is filled with water. The user pumps air out of the container to create a vacuum. A slender nozzle and hose allow the user to spray in hard-to-reach places.

High-Pressure Water

This method consists of a high-pressure pump, an operator controlled directional nozzle, and a high-pressure hose. Operating pressure usually ranges from 340 to 680 atmospheres (atm) and flow rates usually range from 20 to 140 liters per minute.

Ultra-High-Pressure Water

This system produces a water jet that is pressured from 1,000 to 4,000 atmospheres. This ultra-high-pressure spray can remove tightly-adhered surface films. The water velocity ranges from 500 meters/second (m/s) (1,000 atm) to 900 m/s (4,000 atm). Additives can be used to enhance the cleaning action.

Rinsing

Contaminants are removed by rinsing through dilution, physical attraction, and solubilization.

Damp Cloth Removal

In some instances, due to sensitive, non-waterproof equipment or due to the unlikelihood of equipment being contaminated, it is not necessary to conduct an extensive decontamination procedure. For example, air sampling pumps hooked on a fence, placed on a drum, or wrapped in plastic bags are not likely to become heavily contaminated. A damp cloth should be used to wipe off contaminants which may have adhered to equipment through airborne contaminants or from surfaces upon which the equipment was set.

Disinfection/Sterilization

Disinfectants are a practical means of inactivating infectious agents. Unfortunately, standard sterilization methods are impractical for large equipment. This method of decontamination is typically performed off-site.

## 7.2 Field Sampling Equipment Decontamination Procedures

The decontamination line is setup so that the first station is used to clean the most contaminated item. It progresses to the last station where the least contaminated item is cleaned. The spread of contaminants is further reduced by separating each decontamination station by a minimum of three (3) feet. Ideally, the contamination should decrease as the equipment progresses from one station to another farther along in the line.

A site is typically divided up into the following boundaries: Hot Zone or Exclusion Zone (EZ), the Contamination Reduction Zone (CRZ), and the Support or Safe Zone (SZ). The decontamination line should be setup in the Contamination Reduction Corridor (CRC) which is in the CRZ. Figure 1 (Appendix B) shows a typical contaminant reduction zone layout. The CRC controls access into and out of the exclusion zone and confines decontamination activities to a limited area. The CRC boundaries should be conspicuously marked. The far end is the hotline, the boundary between the exclusion zone and the contamination reduction zone. The size of the decontamination corridor depends on the number of stations in the decontamination process, overall dimensions of the work zones, and amount of space available at the site. Whenever possible, it should be a straight line.

Anyone in the CRC should be wearing the level of protection designated for the decontamination crew. Another corridor may be required for the entry and exit of heavy equipment. Sampling and monitoring equipment and sampling supplies are all maintained outside of the CRC. Personnel don their equipment away from the CRC and enter the exclusion zone through a separate access control point at the hotline. One person (or more) dedicated to decontaminating equipment is recommended.

### 7.2.1 Decontamination Setup

Starting with the most contaminated station, the decontamination setup should be as follows:

Station 1: Segregate Equipment Drop

Place plastic sheeting on the ground (Figure 2, Appendix B). Size will depend on amount of

equipment to be decontaminated. Provide containers lined with plastic if equipment is to be segregated. Segregation may be required if sensitive equipment or mildly contaminated equipment is used at the same time as equipment which is likely to be heavily contaminated.

Station 2: Physical Removal With A High-Pressure Washer (Optional)

As indicated in 7.1.2, a high-pressure wash may be required for compounds which are difficult to remove by washing with brushes. The elevated temperature of the water from the high-pressure washers is excellent at removing greasy/oily compounds. High pressure washers require water and electricity.

A decontamination pad may be required for the high-pressure wash area. An example of a wash pad may consist of an approximately 1 1/2 foot-deep basin lined with plastic sheeting and sloped to a sump at one corner. A layer of sand can be placed over the plastic and the basin is filled with gravel or shell. The sump is also lined with visqueen and a barrel is placed in the hole to prevent collapse. A sump pump is used to remove the water from the sump for transfer into a drum.

Typically heavy machinery is decontaminated at the end of the day unless site sampling requires that the machinery be decontaminated frequently. A separate decontamination pad may be required for heavy equipment.

Station 3: Physical Removal With Brushes And A Wash Basin

Prior to setting up Station 3, place plastic sheeting on the ground to cover areas under Station 3 through Station 10.
Fill a wash basin, a large bucket, or child's swimming pool with non-phosphate detergent and tap water. Several bottle and bristle brushes to physically remove contamination should be dedicated to this station . Approximately 10 - 50 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 4: Water Basin

Fill a wash basin, a large bucket, or child's swimming pool with tap water. Several bottle and bristle brushes should be dedicated to this station. Approximately 10-50 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 5: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to contain the water during the rinsing process. Approximately 10-20 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 6: Nitric Acid Sprayers

Fill a spray bottle with 10% nitric acid. An acid rinse may not be required if inorganics are not a contaminant of concern. The amount of acid will depend on the amount of equipment to be decontaminated. Provide a 5-gallon bucket or basin to collect acid during the rinsing process.

Station 7: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 8: Organic Solvent Sprayers

Fill a spray bottle with an organic solvent. After each solvent rinse, the equipment should be rinsed with distilled/deionized water and air dried. Amount of solvent will depend on the amount of equipment to decontaminate. Provide a 5-gallon bucket or basin to collect the solvent during the rinsing process.

Solvent rinses may not be required unless organics are a contaminant of concern, and may be eliminated from the station sequence.

Station 9: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 10: Clean Equipment Drop

Lay a clean piece of plastic sheeting over the bottom

plastic layer. This will allow easy removal of the plastic in the event that it becomes dirty. Provide aluminum foil, plastic, or other protective material to wrap clean equipment.

### 7.2.2 Decontamination Procedures

Station 1: Segregate Equipment Drop

Deposit equipment used on-site (i.e., tools, sampling devices and containers, monitoring instruments radios, clipboards, etc.) on the plastic drop cloth/sheet or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross contamination. Loose-leaf sampling data sheets or maps can be placed in plastic zip lock bags if contamination is evident.

Station 2: Physical Removal With A High-Pressure Washer (Optional)

Use high pressure wash on grossly contaminated equipment. Do not use high- pressure wash on sensitive or non-waterproof equipment.

Station 3: Physical Removal With Brushes And A Wash Basin

Scrub equipment with soap and water using bottle and bristle brushes. Only sensitive equipment (i.e., radios, air monitoring and sampling equipment) which is waterproof should be washed. Equipment which is not waterproof should have plastic bags removed and wiped down with a damp cloth. Acids and organic rinses may also ruin sensitive equipment. Consult the manufacturers for recommended decontamination solutions.

Station 4: Equipment Rinse

Wash soap off of equipment with water by immersing the equipment in the water while brushing. Repeat as many times as necessary.

Station 5: Low-Pressure Rinse

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 6: Nitric Acid Sprayers ( required only if metals are a contaminant of concern)

Using a spray bottle rinse sampling equipment with nitric acid. Begin spraying (inside and outside) at one end of the equipment allowing the acid to drip to the other end into a 5-gallon bucket. A rinsate blank may be required at this station. Refer to Section 9.

Station 7: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 8: Organic Solvent Sprayers

Rinse sampling equipment with a solvent. Begin spraying (inside and outside) at one end of the equipment allowing the solvent to drip to the other end into a 5-gallon bucket. Allow the solvent to evaporate from the equipment before going to the next station. A QC rinsate sample may be required at this station.

Station 9: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure washer.

Station 10 : Clean Equipment Drop

Lay clean equipment on plastic sheeting. Once air dried, wrap sampling equipment with aluminum foil, plastic, or other protective material.

### 7.2.3 Post Decontamination Procedures

1. Collect high-pressure pad and heavy equipment decontamination area liquid and waste and store in appropriate drum or container. A sump pump can aid in the collection process. Refer to the Department of Transportation (DOT) requirements for appropriate containers based on the contaminant of concern.

2. Collect high-pressure pad and heavy equipment decontamination area solid waste and store in appropriate drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

3. Empty soap and water liquid wastes from basins and buckets and store in appropriate

drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

4. Empty acid rinse waste and place in appropriate container or neutralize with a base and place in appropriate drum. pH paper or an equivalent pH test is required for neutralization. Consult DOT requirements for appropriate drum for acid rinse waste.

5. Empty solvent rinse sprayer and solvent waste into an appropriate container. Consult DOT requirements for appropriate drum for solvent rinse waste.

6. Using low-pressure sprayers, rinse basins, and brushes. Place liquid generated from this process into the wash water rinse container.

7. Empty low-pressure sprayer water onto the ground.

8. Place all solid waste materials generated from the decontamination area (i.e., gloves and plastic sheeting, etc.) in an approved DOT drum. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

9. Write appropriate labels for waste and make arrangements for disposal. Consult DOT regulations for the appropriate label for each drum generated from the decontamination process.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITYASSURANCE/ QUALITY CONTROL

A rinsate blank is one specific type of quality control sample associated with the field decontamination process. This sample will provide information on the effectiveness of the decontamination process employed in the field.

Rinsate blanks are samples obtained by running analyte free water over decontaminated sampling equipment to test for residual contamination. The blank water is collected in sample containers for handling, shipment, and analysis. These samples are treated identical to samples collected that day. A rinsate blank is used to assess cross contamination brought about by improper decontamination procedures. Where dedicated sampling equipment is not utilized, collect one rinsate blank per day per type of sampling device samples to meet QA2 and QA3 objectives.

If sampling equipment requires the use of plastic tubing it should be disposed of as contaminated and replaced with clean tubing before additional sampling occurs.

## 10.0 DATA VALIDATION

Results of quality control samples will be evaluated for contamination. This information will be utilized to qualify the environmental sample results in accordance with the project's data quality objectives.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow OSHA, U.S. EPA, corporate, and other applicable health and safety procedures.

Decontamination can pose hazards under certain circumstances. Hazardous substances may be incompatible with decontamination materials. For example, the decontamination solution may react with contaminants to produce heat, explosion, or toxic products. Also, vapors from decontamination solutions may pose a direct health hazard to workers by inhalation, contact, fire, or explosion.

The decontamination solutions must be determined to be acceptable before use. Decontamination materials may degrade protective clothing or equipment; some solvents can permeate protective clothing. If decontamination materials do pose a health hazard, measures should be taken to protect personnel or substitutions should be made to eliminate the hazard. The choice of respiratory protection based on contaminants of concern from the site may not be appropriate for solvents used in the decontamination process.

Safety considerations should be addressed when using abrasive and non-abrasive decontamination

equipment. Maximum air pressure produced by abrasive equipment could cause physical injury. Displaced material requires control mechanisms.

Material generated from decontamination activities requires proper handling, storage, and disposal. Personal Protective Equipment may be required for these activities.

Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard (i.e., acetone, alcohol, and trisodiumphosphate).

In some jurisdictions, phosphate containing detergents (i.e., TSP) are banned.

## 12.0 REFERENCES


Field Sampling Procedures Manual, New Jersey Department of Environmental Protection, February, 1988.

A Compendium of Superfund Field Operations Methods, EPA 540/p-87/001.

Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual, USEPA Region IV, April 1, 1986.

Guidelines for the Selection of Chemical Protective Clothing, Volume 1, Third Edition, American Conference of Governmental Industrial Hygienists, Inc., February, 1987.

Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, NIOSH/OSHA/USCG/EPA, October, 1985.

# APPENDIX A

Table

Table 1. Soluble Contaminants and Recommended Solvent Rinse

| TABLE 1<br>Soluble Contaminants and Recommended Solvent Rinse | | |
|---|---|---|
| SOLVENT[1] | EXAMPLES OF SOLVENTS | SOLUBLE CONTAMINANTS |
| Water | Deionized water<br>Tap water | Low-chain hydrocarbons<br>Inorganic compounds<br>Salts<br>Some organic acids and other polar compounds |
| Dilute Acids | Nitric acid<br>Acetic acid<br>Boric acid | Basic (caustic) compounds (e.g., amines and hydrazines) |
| Dilute Bases | Sodium bicarbonate (e.g., soap detergent) | Acidic compounds<br>Phenol<br>Thiols<br>Some nitro and sulfonic compounds |
| Organic Solvents [2] | Alcohols<br>Ethers<br>Ketones<br>Aromatics<br>Straight chain alkalines (e.g., hexane)<br>Common petroleum products (e.g., fuel, oil, kerosene) | Nonpolar compounds (e.g., some organic compounds) |
| Organic Solvent[2] | Hexane | PCBs |

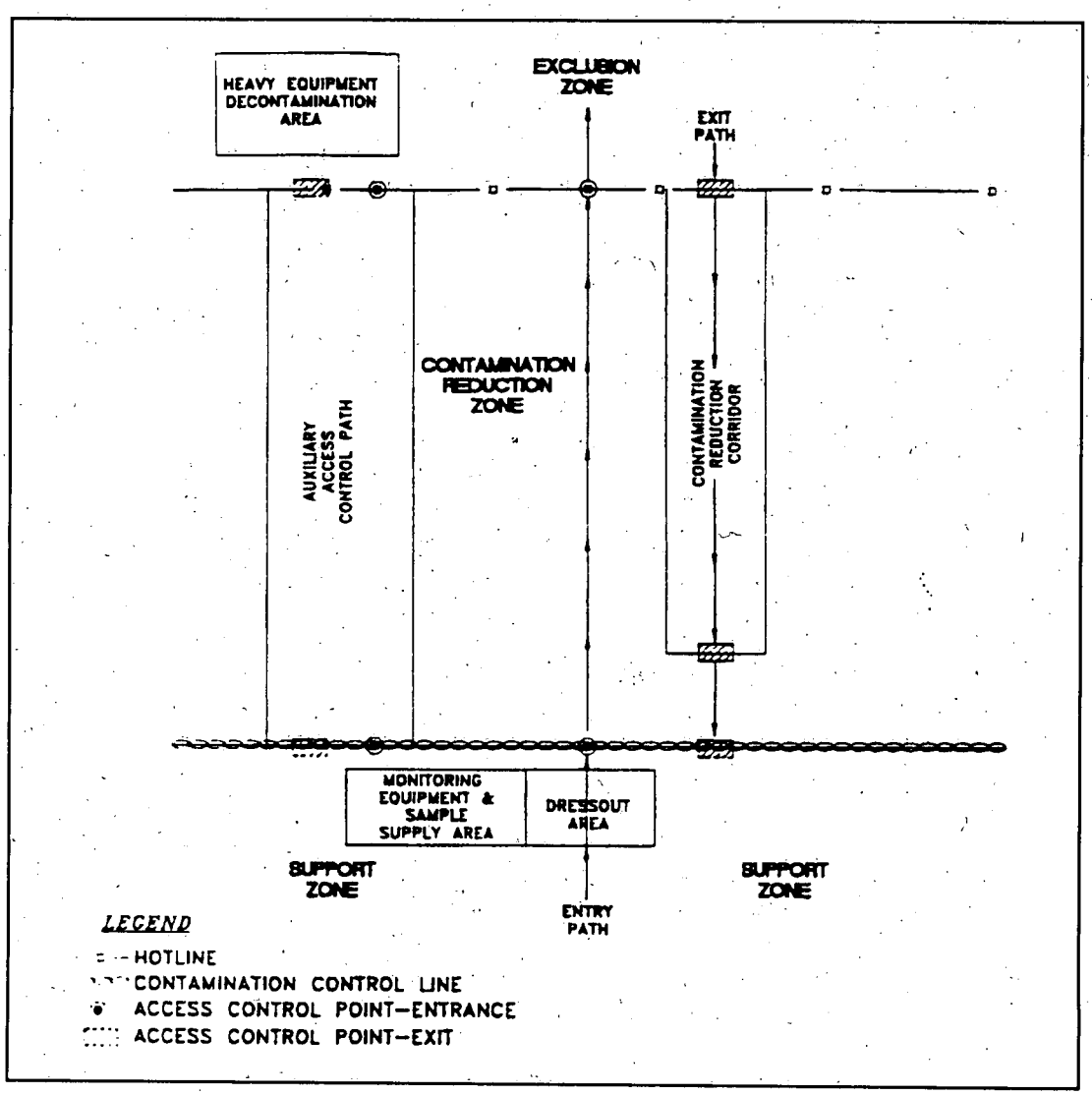
[1] - Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard

[2] - WARNING: Some organic solvents can permeate and/or degrade the protective clothing

# APPENDIX B

## Figures

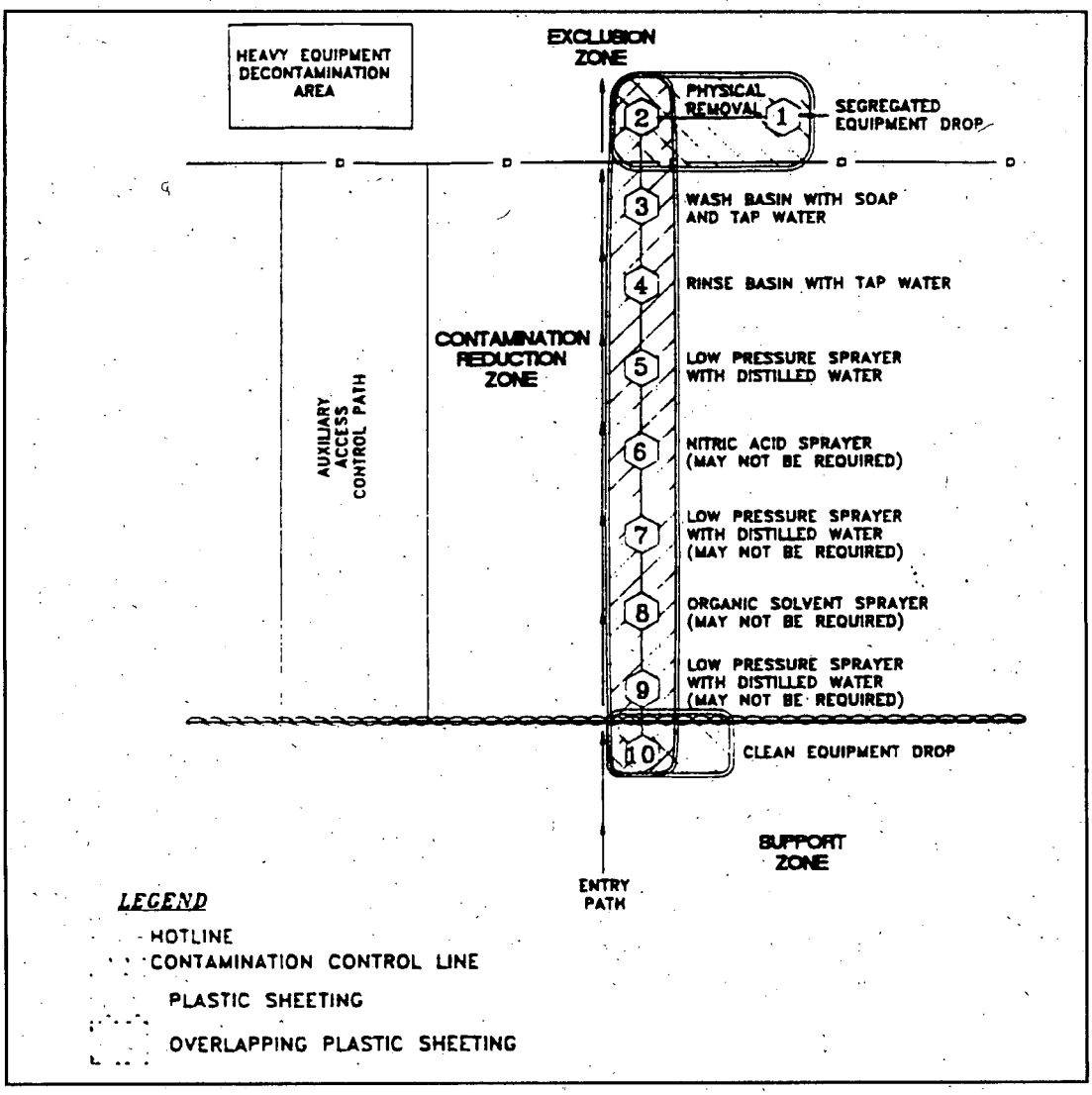
Figure 1. Contamination Reduction Zone Layout



## APPENDIX B (Cont'd.)

Figures

Figure 2. Decontamination Layout



# GROUNDWATER WELL SAMPLING

SOP#: 2007
DATE: 01/26/95
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

The objective of this standard operating procedure (SOP) is to provide general reference information on sampling of ground water wells. This guideline is primarily concerned with the collection of water samples from the saturated zone of the subsurface. Every effort must be made to ensure that the sample is representative of the particular zone of water being sampled. These procedures are designed to be used in conjunction with analyses for the most common types of ground water contaminants (e.g., volatile and semi-volatile organic compounds, pesticides, metals, biological parameters).

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

In order to obtain a representative groundwater sample for chemical analysis it is important to remove stagnant water in the well casing and the water immediately adjacent to the well before collection of the sample. This may be achieved with one of a number of instruments. The most common of these are the bailer, submersible pump, non-contact gas bladder pump, inertia pump and suction pump. At a minimum, three well volumes should be purged, if possible. Equipment must be decontaminated prior to use and between wells. Once purging is completed and the correct laboratory-cleaned sample containers have been prepared, sampling may proceed. Sampling may be conducted with any of the above instruments, and need not be the same as the device used for purging. Care should be taken when choosing the sampling device as some will affect the integrity of the sample. Sampling should occur in a progression from the least to most contaminated well, if this information is known.

The growing concern over the past several years over low levels of volatile organic compounds in water supplies has led to the development of highly sophisticated analytical methods that can provide detection limits at part per trillion levels. While the laboratory methods are extremely sensitive, well controlled and quality assured, they cannot compensate for a poorly collected sample. The collection of a sample should be as sensitive, highly developed and quality assured as the analytical procedures.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The type of analysis for which a sample is being collected determines the type of bottle, preservative, holding time, and filtering requirements. Samples should be collected directly from the sampling device into appropriate laboratory cleaned containers. Check that a Teflon liner is present in the cap, if required. Attach a sample identification label. Complete a field data sheet, a chain of custody form, and record all pertinent data in the site logbook.

Samples shall be appropriately preserved, labelled, logged, and placed in a cooler to be maintained at 4°C. Samples must be shipped well before the holding time is up and ideally should be shipped within 24 hours of sample collection. It is imperative that samples be shipped or delivered daily to the analytical laboratory in order to maximize the time available for the laboratory to perform the analyses. The bottles should be shipped with adequate packing and cooling to ensure that they arrive intact.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must remain to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

Treatment of the sample with sodium thiosulfate preservative is required only if there is residual chlorine in the water that could cause free radical chlorination and change the identity of the original contaminants. It should not be used if there is no chlorine in the water.

Holding time for volatiles analysis is seven days. It is imperative that the sample be shipped or delivered daily to the analytical laboratory. The bottles must be shipped on their sides to aid in maintaining the airtight seal during shipment, with adequate packing and cooling to ensure that they arrive intact.

For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies; field kit for chlorine, preservatives, Parafilm, foam sleeves and coolers. Due to the extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

### 4.1 General

The primary goal in performing ground water sampling is to obtain a representative sample of the ground water body. Analysis can be compromised by field personnel in two primary ways: (1) taking an unrepresentative sample, or (2) by incorrect handling of the sample. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utilizing trained field personnel.

### 4.2 Purging

In a nonpumping well, there will be little or no vertical mixing of the water, and stratification will occur. The well water in the screened section will mix with the ground water due to normal flow patterns, but the well water above the screened section will remain isolated, become stagnant, and may lack the contaminants representative of the ground water. Persons sampling should realize that stagnant water may contain foreign material inadvertently or deliberately introduced from the surface, resulting in an unrepresentative sample. To safeguard against collecting nonrepresentative stagnant water, the following guidelines and techniques should be adhered to during sampling:

1. As a general rule, all monitor wells should be pumped or bailed prior to sampling. Purge water should be containerized on site or handled as specified in the site specific project plan. Evacuation of a minimum of one volume of water in the well casing, and preferably three to five volumes, is recommended for a representative sample. In a high-yielding ground water formation and where there is no stagnant water in the well above the screened section, evacuation prior to sample withdrawal is not as critical. However, in all cases where the monitoring data is to be used for enforcement actions, evacuation is recommended.

2. When purging with a pump (not a bailer), the pump should be set at the screened interval, or if the well is an open-rock well, it should be set at the same depth the sample will be collected. When sampling a screened well, the sample should also be collected from the same depth the pump was set at.

3. The well should be sampled as soon as possible after purging.

4. Analytical parameters typically dictate whether the sample should be collected through the purging device, or through a separate sampling instrument.

5. For wells that can be pumped or bailed to dryness with the equipment being used, the well should be evacuated and allowed to

recover prior to collecting a sample. If the recovery rate is fairly rapid and time allows, evacuation of more than one volume of water is preferred. If recovery is slow, sample the well upon recovery after one evacuation.

6. A non-representative sample can also result from excessive pre-pumping of the monitoring well. Stratification of the leachate concentration in the ground water formation may occur, or heavier-than-water compounds may sink to the lower portions of the aquifer. Excessive pumping can dilute or increase the contaminant concentrations from what is representative of the sampling point of interest.

## 4.3 Materials

Materials of construction for samplers and evacuation equipment (bladders, pump, bailers, tubing, etc.) should be limited to stainless steel, Teflon$^R$, and glass in areas where concentrations are expected to be at or near the detection limit. The tendency of organics to leach into and out of many materials make the selection of materials critical for trace analyses. The use of plastics, such as PVC or polyethylene, should be avoided when analyzing for organics. However, PVC may be used for evacuation equipment as it will not come in contact with the sample, and in highly contaminated wells, disposable equipment (i.e., polypropylene bailers) may be appropriate to avoid cross-contamination.

Materials of construction (bladders/ pumps, bailers, tubing, etc.) suitable for collecting and handling Volatile Organic Samples should be limited to stainless steel, Teflon and glass in areas which detection limit range concentrations are expected. The tendency of organics to leach into and out of many materials, make the selection of materials critical for these trace analyses. The use of plastics, e.g., PVC etc., should be avoided. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utlization of trained personnel.

## 4.4 Advantages/Disadvantages of Certain Equipment

### 4.4.1 Bailers

Advantages

- Only practical limitations on size and materials
- No power source needed
- Portable
- Inexpensive, so it can be dedicated and hung in a well, thereby reducing the chances of cross contamination
- Minimal outgassing of volatile organics while sample is in bailer
- Readily available
- Removes stagnant water first
- Rapid, simple method for removing small volumes of purge water

Disadvantages

- Time-consuming to flush a large well of stagnant water
- Transfer of sample may cause aeration
- Stoppers at the bottom of the bailer usually leak thus the bailer must be brought to the surface rapidly
- If the bailer is allowed to hit the bottom of the well boring, gravel can displace the ball valve not allowing the bailer to hold water

### 4.4.2 Submersible Pumps

Advantages

- Portable and can be transported to several wells
- Depending upon the size of the pump and the pumping depths, relatively high pumping rates are possible
- Generally very reliable and does not require priming

Disadvantages

- Potential for effects on analysis of trace organics
- Heavy and cumbersome to deal with, particularly in deeper wells
- Expensive
- Power source needed
- Sediment in water may cause problems with the pumps
- Impractical in low yielding or shallow wells

### 4.4.3 Non-Contact Gas Bladder Pumps

Advantages

- Maintains integrity of sample
- Easy to use
- Can sample from discrete locations within the monitor well

Disadvantages

- Difficulty in cleaning, though dedicated tubing and bladder may be used
- Only useful to about 100 feet
- Supply of gas for operation, gas bottles and/or compressors are often difficult to obtain and are cumbersome
- Relatively low pumping rates
- Requires air compressor or pressurized gas source and control box

### 4.4.4 Suction Pumps

Advantages

- Portable, inexpensive, and readily available

Disadvantages

- Restricted to areas with water levels within 20 to 25 feet of the ground surface
- Vacuum can cause loss of dissolved gasses and volatile organics
- Pump must be primed and vacuum is often difficult to maintain during initial stages of pumping

### 4.4.5 Inertia Pumps

Advantages

- Portable, inexpensive, and readily available
- Offers a rapid method for purging relatively shallow wells

Disadvantages

- Restricted to areas with water levels within 70 feet of the ground surface
- May be time consuming to purge wells with these manual pumps
- Labor intensive
- WaTerra pumps are only effective in 2-inch diameter wells

## 5.0 EQUIPMENT APPARATUS

## 5.1 Equipment Checklist

### 5.1.1 General

- Water level indicator
  - electric sounder
  - steel tape
  - transducer
  - reflection sounder
  - airline
- Depth sounder
- Appropriate keys for well cap locks
- Steel brush
- HNU or OVA (whichever is most appropriate)
- Logbook
- Calculator
- Field data sheets and samples labels

- Chain of custody records and seals
- Sample containers
- Engineer's rule
- Sharp knife (locking blade)
- Tool box (to include at least: screwdrivers, pliers, hacksaw, hammer, flashlight, adjustable wrench)
- Leather work gloves
- Appropriate Health & Safety gear
- 5-gallon pail
- Plastic sheeting
- Shipping containers
- Packing materials
- Bolt cutters
- Ziploc plastic bags
- Containers for evacuation liquids
- Decontamination solutions
- Tap water
- Non phosphate soap
- Several brushes
- Pails or tubs
- Aluminum foil
- Garden sprayer
- Preservatives
- Distilled or deionized water
- Fire extinguisher (if using a generator for your power source)

### 5.1.2 Bailers

- Clean, decontaminated bailers of appropriate size and construction material
- Nylon line, enough to dedicate to each well
- Teflon coated bailer wire
- Sharp knife
- Aluminum foil (to wrap clean bailers)
- Five gallon bucket

### 5.1.3 Submersible Pump

- Pump(s)
- Generator (110, 120, or 240 volt) or 12 volt battery if inaccessible to field vehicle - amp meter is useful
- 1" black PVC coil tubing - enough to dedicate to each well
- Hose clamps
- Safety cable
- Tool box supplement
  - pipe wrenches
  - wire strippers
  - electrical tape
  - heat shrink
  - hose connectors
  - Teflon tape
- Winch, pulley or hoist
- Gasoline for generator/gas can
- Flow meter with gate valve
- 1" nipples and various plumbing (i.e., pipe connectors)
- Control box (if necessary)

### 5.1.4 Non-Gas Contact Bladder Pump

- Non-gas contact bladder pump
- Compressor or nitrogen gas tank
- Batteries and charger
- Teflon tubing - enough to dedicate to each well
- Swagelock fitting
- Toolbox supplements - same as submersible pump
- Control box (if necessary)

### 5.1.5 Suction Pump

- Pump
- 1" black PVC coil tubing - enough to dedicate to each well
- Gasoline - if required
- Toolbox
- Plumbing fittings
- Flow meter with gate valve

### 5.1.6 Inertia Pump

- Pump assembly (WaTerra pump, piston pump)
- Five gallon bucket

## 6.0 REAGENTS

Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

## 7.0 PROCEDURE

### 7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed (i.e, diameter and depth of wells to be sampled).

2. Obtain necessary sampling and monitoring equipment, appropriate to type of contaminant being investigated. For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies; field kit for chlorine, preservatives, Parafilm, foam sleeves and coolers. Due to extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.

3. Decontaminate or preclean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Identify and mark all sampling locations.

### 7.2 Field Preparation

1. Start at the least contaminated well, if known.

2. Lay plastic sheeting around the well to minimize likelihood of contamination of equipment from soil adjacent to the well.

3. Remove locking well cap, note location, time of day, and date in field notebook or appropriate log form.

4. Remove well casing cap.

5. Screen headspace of well with an appropriate monitoring instrument to determine the presence of volatile organic compounds and record in site logbook.

6. Lower water level measuring device or equivalent (i.e., permanently installed transducers or airline) into well until water surface is encountered.

7. Measure distance from water surface to reference measuring point on well casing or protective barrier post and record in site logbook. Alternatively, if no reference point, note that water level measurement is from top of steel casing, top of PVC riser pipe, from ground surface, or some other position on the well head.

   If floating organics are of concern, this can be determined by measuring the water level with an oil/water interface probe which measures floating organics.

8. Measure total depth of well (at least twice to confirm measurement) and record in site logbook or on field data sheet.

9. Calculate the volume of water in the well and the volume to be purged using the calculations in Section 8.0.

10. Select the appropriate purging and sampling equipment.

11. If residual chlorine is suspected, use the Hach Field Test Kit for chlorine to determine if there is residual chlorine in the water to be sampled. If there is, treat the sample vial with a crystal of sodium thiosulfate prior to sample collection.

### 7.3 Purging

The amount of flushing a well receives prior to sample collection depends on the intent of the monitoring program as well as the hydrogeologic conditions. Programs where overall quality determination of water resources are involved may require long pumping periods to obtain a sample that is representative of a large volume of that aquifer. The pumped volume can be determined prior to sampling so that the sample is

a collected after a known volume of the water is evacuated from the aquifer, or the well can be pumped until the stabilization of parameters such as temperature, electrical conductance, pH, or turbidity has occurred.

However, monitoring for defining a contaminant plume requires a representative sample of a small volume of the aquifer. These circumstances require that the well be pumped enough to remove the stagnant water but not enough to induce flow from other areas. Generally, three well volumes are considered effective, or calculations can be made to determine, on the basis of the aquifer parameters and well dimensions, the appropriate volume to remove prior to sampling.

During purging, water level measurements may be taken regularly at 15-30 second intervals. This data may be used to compute aquifer transmissivity and other hydraulic characteristics. The following well evacuation devices are most commonly used. Other evacuation devices are available, but have been omitted in this discussion due to their limited use.

### 7.3.1 Bailers

Bailers are the simplest purging device used and have many advantages. They generally consist of a rigid length of tube, usually with a ball check-valve at the bottom. A line is used to lower the bailer into the well and retrieve a volume of water. The three most common types of bailer are PVC, Teflon, and stainless steel.

This manual method of purging is best suited to shallow or narrow diameter wells. For deep, larger diameter wells which require evacuation of large volumes of water, other mechanical devices may be more appropriate.

#### 7.3.1.1 Operation

Equipment needed will include a clean decontaminated bailer, Teflon or nylon line, a sharp knife, and plastic sheeting.

1. Determine the volume of water to be purged as described in 8.0, calculations.

2. Lay plastic sheeting around the well to prevent contamination of the bailer line with foreign materials.

3. Attach the line to the bailer and slowly lower until the bailer is completely submerged, being careful not to drop the bailer to the water, causing turbulence and the possible loss of volatile organic contaminants.

4. Pull bailer out ensuring that the line either falls onto a clean area of plastic sheeting or never touches the ground.

5. Empty the bailer into a pail until full to determine the number of bails necessary to achieve the required purge volume.

6. Thereafter, pour the water into a container and dispose of purge waters as specified in the site specific sampling plan.

### 7.3.2 Submersible Pumps

The use of submersible pumps for sample collection is permissible provided they are constructed of suitably noncontaminating materials. The chief drawback, however, is the difficulty avoiding cross-contamination between wells. Although some units can be disassembled easily to allow surfaces contacted by contaminants to be cleaned, field decontamination may be difficult and require solvents that can affect sample analysis. The use of submersible pumps in multiple well-sampling programs, therefore, should be carefully considered against other sampling mechanisms (bailers, bladder pumps). In most cases, a sample can be collected by bailer after purging with a submersible pump, however, submersible pumps may be the only practical sampling device for extremely deep wells (greater than 300 feet of water). Under those conditions, dedicated pump systems should be installed to eliminate the potential for cross-contamination of well samples.

Submersible pumps generally use one of two types of power supplies, either electric or compressed gas or air. Electric powered pumps can run off a 12 volt DC rechargeable battery, or a 110 or 220 volt AC power supply. Those units powered by compressed air normally use a small electric or gas-powered air compressor. They may also utilize compressed gas (i.e., nitrogen) from bottles. Different size pumps are available for different depth or diameter monitoring wells.

#### 7.3.2.1 Operation

1. Determine the volume of water to be purged as described in 8.0 Calculations.

2. Lay plastic sheeting around the well to prevent contamination of pumps, hoses or lines with foreign materials.

3. Assemble pump, hoses and safety cable, and lower the pump into the well. Make sure the pump is deep enough so all the water is not evacuated. (Running the pump without water may cause damage.)

4. Attach flow meter to the outlet hose to measure the volume of water purged.

5. Use a ground fault circuit interrupter (GFCI) or ground the generator to avoid possible electric shock.

6. Attach power supply, and purge the well until the specified volume of water has been evacuated (or until field parameters, such as temperature, pH, conductivity, etc, have stabilized). Do not allow the pump to run dry. If the pumping rate exceeds the well recharge rate, lower the pump further into the well, and continue pumping.

7. Collect and dispose of purge waters as specified in the site specific sampling plan.

### 7.3.3 Non-Contact Gas Bladder Pumps

For this procedure, an all stainless-steel and Teflon Middleburg-squeeze bladder pump (e.g., IEA, TIMCO, Well Wizard, Geoguard, and others) is used to provide the least amount of material interference to the sample (Barcelona, 1985). Water comes into contact with the inside of the bladder (Teflon) and the sample tubing, also Teflon, that may be dedicated to each well. Some wells may have permanently installed bladder pumps, (i.e., Well Wizard, Geoguard), that will be used to sample for all parameters.

#### 7.3.3.1 Operation

1. Assemble Teflon tubing, pump and charged control box.

2. Procedure for purging with a bladder pump is the same as for a submersible pump (Section 7.3.2.1).

3. Be sure to adjust flow rate to prevent violent jolting of the hose as sample is drawn in.

### 7.3.4 Suction Pumps

There are many different types of suction pumps. They include: centrifugal, peristaltic and diaphragm. Diaphragm pumps can be used for well evacuation at a fast pumping rate and sampling at a low pumping rate. The peristaltic pump is a low volume pump that uses rollers to squeeze the flexible tubing thereby creating suction. This tubing can be dedicated to a well to prevent cross contamination. Peristaltic pumps, however, require a power source.

#### 7.3.4.1 Operation

1. Assembly of the pump, tubing, and power source if necessary.

2. Procedure for purging with a suction pump is exactly the same as for a submersible pump (Section 7.3.2.1).

### 7.3.5 Inertia Pumps

Inertia pumps such as the WaTerra pump and piston pump, are manually operated. They are most appropriate to use when wells are too deep to bail by hand, or too shallow or narrow (or inaccessible) to warrant an automatic (submersible, etc.) pump. These pumps are made of plastic and may be either decontaminated or discarded.

#### 7.3.5.1 Operation

1. Determine the volume of water to be purged as described in 8.0, Calculations.

2. Lay plastic sheeting around the well to prevent contamination of pumps or hoses with foreign materials.

3. Assemble pump and lower to the appropriate depth in the well.

4. Begin pumping manually, discharging water into a 5 gallon bucket (or other graduated vessel). Purge until specified volume of water has been evacuated (or until field parameters such as temperature, pH,

conductivity, etc. have stabilized).

5. Collect and dispose of purge waters as specified in the site specific project plan.

## 7.4 Sampling

Sample withdrawal methods require the use of pumps, compressed air, bailers, and samplers. Ideally, purging and sample withdrawal equipment should be completely inert, economical to manufacture, easily cleaned, sterilized, reusable, able to operate at remote sites in the absence of power resources, and capable of delivering variable rates for sample collection.

There are several factors to take into consideration when choosing a sampling device. Care should be taken when reviewing the advantages or disadvantages of any one device. It may be appropriate to use a different device to sample than that which was used to purge. The most common example of this is the use of a submersible pump to purge and a bailer to sample.

### 7.4.1 Bailers

The positive-displacement volatile sampling bailer is perhaps the most appropriate for collection of water samples for volatile analysis. Other bailer types (messenger, bottom fill, etc.) are less desirable, but may be mandated by cost and site conditions.

#### 7.4.1.1 Operation

1. Surround the monitor well with clean plastic sheeting. If using the GPI bailer, insert a vial into the claim and assemble the unit.

2. Attach a line to a clean decontaminated bailer.

3. Lower the bailer slowly and gently into the well, taking care not to shake the casing sides or to splash the bailer into the water. Stop lowering at a point adjacent to the screen.

4. Allow bailer to fill and then slowly and gently retrieve the bailer from the well avoiding contact with the casing, so as not to knock flakes of rust or other foreign materials into the bailer. If using the GPI bailer for collecting volatile organic samples, once at the surface, remove the bailer from the cable. Carefully open the GPI bailer unit and remove the vial. Begin slowly pouring from the bailer, and collect the duplicate samples from the midstream sample.

5. Remove the cap from the sample container and place it on the plastic sheet or in a location where it won't become contaminated. See Section 7.7 for special considerations on VOA samples.

6. Begin slowly pouring from the bailer.

7. Filter and preserve samples as required by sampling plan.

8. Cap the sample container tightly and place prelabeled sample container in a carrier.

9. Replace the well cap.

10. Log all samples in the site logbook and on field data sheets and label all samples.

11. Package samples and complete necessary paperwork.

12. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

### 7.4.2 Submersible Pumps

Although it is recommended that samples not be collected with a submersible pump due to the reasons stated in Section 4.4.2, there are some situations where they may be used.

#### 7.4.2.1 Operation

1. Allow the monitor well to recharge after purging, keeping the pump just above screened section.

2. Attach gate valve to hose (if not already fitted), and reduce flow of water to a manageable sampling rate.

3. Assemble the appropriate bottles.

4. If no gate valve is available, run the water

down the side of a clean jar and fill the sample bottles from the jar.

5. Cap the sample container tightly and place prelabeled sample container in a carrier.

6. Replace the well cap.

7. Log all samples in the site logbook and on the field data sheets and label all samples.

8. Package samples and complete necessary paperwork.

9. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.

10. Upon completion, remove pump and assembly and fully decontaminate prior to setting into the next sample well. Dedicate the tubing to the hole.

### 7.4.3 Non-Contact Gas Bladder Pumps

The use of a non-contact gas positive displacement bladder pump is often mandated by the use of dedicated pumps installed in wells. These pumps are also suitable for shallow (less than 100 feet) wells. They are somewhat difficult to clean, but may be used with dedicated sample tubing to avoid cleaning. These pumps require a power supply and a compressed gas supply (or compressor). They may be operated at variable flow and pressure rates making them ideal for both purging and sampling.

Barcelona (1984) and Nielsen (1985) report that the non-contact gas positive displacement pumps cause the least amount of alteration in sample integrity as compared to other sample retrieval methods.

#### 7.4.3.1 Operation

1. Allow well to recharge after purging.

2. Assemble the appropriate bottles.

3. Turn pump on, increase the cycle time and reduce the pressure to the minimum that will allow the sample to come to the surface.

4. Cap the sample container tightly and place prelabeled sample container in a carrier.

5. Replace the well cap.

6. Log all samples in the site logbook and on field data sheets and label all samples.

7. Package samples and complete necessary paperwork.

8. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

9. On completion, remove the tubing from the well and either replace the Teflon tubing and bladder with new dedicated tubing and bladder or rigorously decontaminate the existing materials.

10. Nonfiltered samples shall be collected directly from the outlet tubing into the sample bottle.

11. For filtered samples, connect the pump outlet tubing directly to the filter unit. The pump pressure should remain decreased so that the pressure build up on the filter does not blow out the pump bladder or displace the filter. For the Geotech barrel filter, no actual connections are necessary so this is not a concern.

### 7.4.4 Suction Pumps

In view of the limitations of these type pumps, they are not recommended for sampling purposes.

### 7.4.5 Inertia Pumps

Inertia pumps may be used to collect samples. It is more common, however, to purge with these pumps and sample with a bailer (Section 7.4.1).

#### 7.4.5.1 Operation

1. Following well evacuation, allow the well to recharge.

2. Assemble the appropriate bottles.

3. Since these pumps are manually operated,

the flow rate may be regulated by the sampler. The sample may be discharged from the pump outlet directly into the appropriate sample container.

4. Cap the sample container tightly and place prelabeled sample container in a carrier.

5. Replace the well cap.

6. Log all samples in the site logbook and on field data sheets and label all samples.

7. Package samples and complete necessary paperwork.

8. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.

9. Upon completion, remove pump and decontaminate or discard, as appropriate.

### 7.4.6. Sample Retrieval - Syringe

A limited number of commercial syringe type samplers are available, (IEA, TIMCO, etc.) some are homemade devices. These devices are claimed to provide good quality samples for volatile analysis, but are severly limited in sample volume and are specific to sampling for volatiles. Essentially, they operated with an evacuated chamber that is lowered down the well, and allowed to fill with the pressure of the water. The entire mechanism is then brought to the surface with the sample. The sample may then be transferred to a sample vial, or the entire unit may be sent as the sample container.

1. Evacuate the syringe if necessary, and lower the sampling device to just below the well screen.

2. Remove the constriction from the device and allow the sample to fill the syringe, apply slight suction as necessary.

3. Bring unit to the surface. If necessary, transfer the sample to vials, as outlined in steps 2 through 7 above.

## 7.5 Filtering

For samples requiring filtering, such as total metals analysis, the filter must be decontaminated prior to and between uses. Filters work by two methods. A barrel filter such as the "Geotech" filter works with a bicycle pump, used to build up positive pressure in the chamber containing the sample which is then forced through the filter paper (minimum size 0.45 µm) into a jar placed underneath. The barrel itself is filled manually from the bailer or directly via the hose of the sampling pump. The pressure must be maintained up to 30 $lbs/in^2$ by periodic pumping.

A vacuum type filter involves two chambers; the upper chamber contains the sample and a filter (minimum size 0.45 µm) divides the chambers. Using a hand pump or a Gilian type pump, air is withdrawn from the lower chamber, creating a vacuum and thus causing the sample to move through the filter into the lower chamber where it is drained into a sample jar. Repeated pumping may be required to drain all the sample into the lower chamber. If preservation of the sample is necessary, this should be done after filtering.

## 7.6 Post Operation

After all samples are collected and preserved, the sampling equipment should be decontaminated prior to sampling another well to prevent cross-contamination of equipment and monitor wells between locations.

1. Decontaminate all equipment.

2. Replace sampling equipment in storage containers.

3. Prepare and transport ground water samples to the laboratory. Check sample documentation and make sure samples are properly packed for shipment.

## 7.7 Special Considerations for VOA Sampling

The proper collection of a sample for volatile organics requires minimal disturbance of the sample to limit volatilization and therefore a loss of volatiles from the sample.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must be to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

The following procedures should be followed:

1. Open the vial, set cap in a clean place, and collect the sample during the middle of the cycle. When collecting duplicates, collect both samples at the same time.

2. Fill the vial to just overflowing. Do not rinse the vial, nor excessively overflow it. There should be a convex meniscus on the top of the vial.

3. Check that the cap has not been contaminated (splashed) and carefully cap the vial. Place the cap directly over the top and screw down firmly. Do not overtighten and break the cap.

4. Invert the vial and tap gently. Observe vial for at least ten (10) seconds. If an air bubble appears, discard the sample and begin again. It is imperative that no entrapped air is in the sample vial.

5. Immediately place the vial in the protective foam sleeve and place into the cooler, oriented so that it is lying on its side, not straight up.

6. The holding time for VOAs is seven days. Samples should be shipped or delivered to the laboratory daily so as not to exceed the holding time. Ensure that the samples remain at 4°C, but do not allow them to freeze.

## 8.0 CALCULATIONS

If it is necessary to calculate the volume of the well, utilize the following equation:

$$\textit{Well volume} = nr^2h\ (cf) \qquad [\textit{Equation } 1]$$

where:

| | | |
|---|---|---|
| $n$ | = | pi |
| $r$ | = | radius of monitoring well (feet) |
| $h$ | = | height of the water column (feet) [This may be determined by subtracting the depth to water from the total depth of the well as measured from the same reference point.] |
| $cf$ | = | conversion factor (gal/ft$^3$) = 7.48 gal/ft$^3$ [In this equation, 7.48 gal/ft$^3$ is the necessary conversion factor.] |

Monitor well diameters are typically 2", 3", 4", or 6". Knowing the diameter of the monitor well, there are a number of standard conversion factors which can be used to simplify the equation above.

The volume, in gallons per linear foot, for various standard monitor well diameters can be calculated as follows:

$$v(gal/ft) = nr^2\ (cf) \qquad [\textit{Equation } 2]$$

where:

| | | |
|---|---|---|
| $n$ | = | pi |
| $r$ | = | radius of monitoring well (feet) |
| $cf$ | = | conversion factor (7.48 gal/ft$^3$) |

For a 2" diameter well, the volume per linear foot can be calculated as follows:

$$\textit{vol/linear ft} = nr^2\ (cf) \qquad [\textit{Equation } 2]$$
$$= \mathbf{3.14\ (1/12\ ft)^2\ \ 7.48\ gal/ft^3}$$
$$= \mathbf{0.1632\ gal/ft}$$

Remember that if you have a 2" diameter well, you must convert this to the radius in feet to be able to use the equation.

The conversion factors for the common size monitor wells are as follows:

| Well diameter | 2" | 3" | 4" | 6" |
|---|---|---|---|---|
| Volume (gal/ft.) | 0.1632 | 0.3672 | 0.6528 | 1.4688 |

If you utilize the conversion factors above, Equation

l should be modified as follows:

$$\textit{Well volume} = (h)(cf) \quad [\textit{Equation } 3]$$

where:

$h$ = height of water column (feet)
$cf$ = the conversion factor calculated from Equation 2

The well volume is typically tripled to determine the volume to be purged.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

3. The collection of rinsate blanks is recommended to evaluate potential for cross contamination from the purging and/or sampling equipment.

4. Trip blanks are required if analytical parameters include VOAs.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA or REAC health and safety guidelines. More specifically, depending upon the site specific contaminants, various protective programs must be implemented prior to sampling the first well. The site health and safety plan should be reviewed with specific emphasis placed on the protection program planned for the well sampling tasks. Standard safe operating practices should be followed such as minimizing contact with potential contaminants in both the vapor phase and liquid matrix through the use of respirators and disposable clothing.

When working around volatile organic contaminants:

1. Avoid breathing constituents venting from the well.

2. Pre-survey the well head-space with an FID/PID prior to sampling.

3. If monitoring results indicate organic constituents, sampling activities may be conducted in Level C protection. At a minimum, skin protection will be afforded by disposable protective clothing.

Physical hazards associated with well sampling:

1. Lifting injuries associated with pump and bailers retrieval; moving equipment.

2. Use of pocket knives for cutting discharge hose.

3. Heat/cold stress as a result of exposure to extreme temperatures and protective clothing.

4. Slip, trip, fall conditions as a result of pump discharge.

5. Restricted mobility due to the wearing of protective clothing.

6. Electrical shock associated with use of submersible pumps is possible. Use a GFCI or a copper grounding stake to avoid this problem.

## 12.0 REFERENCES

Barcelona, M.J., Helfrich, J.A., Garske, E.E., and J.P. Gibb, Spring 1984. "A Laboratory Evaluation of Groundwater Sampling Mechanisms," Groundwater

Monitoring Review, 1984 pp. 32-41.

Barcelona, M.J., Helfrich, J.A., and Garske, E.E., "Sampling Tubing Effects on Groundwater Samples", Analy. Chem., Vol. 57, 1985 pp. 460-463.

Driscoll, F.G., Groundwater and Wells (2nd ed.) Johnson Division, UOP Inc., St. Paul, Minnesota, 1986, 1089 pp.

Gibb, J.P., R.M. Schuller, and R.A. Griffin,. Monitoring Well Sampling and Preservation Techniques, EPA-600/9-80-010, 1980. March, 1980.

Instrument Specialties Company, (January). Instruction Manual, Model 2100 Wastewater Sampler, Lincoln, Nebraska, 1980.

Keely, J.F. and Kwasi Boateng, Monitoring Well Installation, Purging and Sampling Techniques - Part I: Conceptualizations, Groundwater V25, No. 3, 1987 pp. 300-313.

Keith, Lawrence H., Principles of Environmental Sampling, American Chemical Society, 1988.

Korte, Nic, and Dennis Ealey,. Procedures for Field Chemical Analyses of Water Samples, U.S. Department of Energy, GJ/TMC-07, Technical Measurements Center, Grand Junction Project Office, 1983.

Korte, Nic, and Peter Kearl,. Procedures for the Collection and Preservation of Groundwater and Surface Water Samples and for the Installation of Monitoring Wells: Second Edition, U.S. Department of Energy, GJ/TMC-08, Technical Measurements Center, Grand Junction Projects Office, 1985.

National Council of the Paper Industry for Air and Stream Improvement, Inc.,. A Guide to Groundwater Sampling, Technical Bulletin No. 362, Madison, New York. January, 1982.

Nielsen, David M. and Yeates, Gillian L., Spring. "A Comparison of Sampling Mechanisms Available for Small-Diameter Groundwater Monitoring Wells," Groundwater Monitoring Review, 1985 pp. 83-99.

Scalf, et al. (M.J. Scalf, McNabb, W. Dunlap, R. Crosby,.and J. Fryberger),. Manual for Groundwater Sampling Procedures. R.S. Kerr Environmental Research Laboratory, Office of Research and Development. 1980, Ada, OK.

Sisk, S.W. NEIC Manual for Ground/Surface Investigations at Hazardous Waste Sites, EPA-330/9-81-002, 1981.

U.S. Department of the Interior, National Handbook of Recommended Methods for Water-Data Acquisition, Reston, Virginia.

U.S. Environmental Protection Agency, 1977. Procedures Manual for Groundwater Monitoring at Solid Waste Disposal Facilities. EPA-530/SW-611. August, 1977.

U.S. Code of Federal Regulations, 49 CFR Parts 100 to 177, Transportation revised November 1, 1985.

U.S. Environmental Protection Agency, 1982. Handbook for Chemical and Sample Preservation of Water and Wastewater, EPA-600/4-82-029, Washington, D.C.

U.S. Environmental Protection Agency, 1983. Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020, Washington, D.C.

U.S. Environmental Protection Agency, 1984. Test Methods for Evaluation of Solid Waste, EPA-SW-846, Second Edition, Washington, D.C.

U.S. Environmental Protection Agency, 1981. Manual of Groundwater Quality Sampling Procedures, EPA-600/2-81-160, Washington, D.C.

U.S. Environmental Protection Agency, 1985. Practical Guide for Groundwater Sampling, EPA-600/2-85/104, September, 1985.

U.S. Environmental Protection Agency, 1986. RCRA Groundwater Monitoring Technical Enforcement Guidance Document, OSWER-9950-1, September, 1986.

Weston, 1987. Standard Operations Procedures for Monitor Well Installation. MOUND IGMP/RIP.

U.S. Environmental Protection Agency, 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA-600/4-82-029, Washington, D.C.

--- 1981. Manual of Groundwater Quality

Sampling Procedures, EPA-600/2-81-160, Washington, D.C.

--- 1985. Practice Guide for Groundwater Sampling, EPA-600/2/85-104, September 1985.

Nielsen, David M. and Yeates, Gillian L., Spring 1985. "A Comparison of Sampling Mechanisms Available for Small-Diameter Groundwater Monitoring Wells," Groundwater Monitoring Review, pp. 83-99.

WESTON, 1987. Standard Operating Procedures for Monitor Well Installation. MOUND IGMP/RIP

Barcelona, M.J. Helfrich, J.A., and Garske, E.E., "Sampling Tubing Effects on Groundwater Samples". 1985, Analy. Chem., Vol. 57, pp. 460-463.

# U. S. EPA ENVIRONMENTAL RESPONSE TEAM

## STANDARD OPERATING PROCEDURES



**SOIL SAMPLING**

CONTENTS



SUPERCEDES: SOP #2012; Revision 0.0; 11/16/94; U.S. EPA Contract 68-C4-0022.

1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe the procedures for the collection of representative soil samples. Sampling depths are assumed to be those that can be reached without the use of a drill rig, direct-push, or other mechanized equipment (except for a back-hoe). Analysis of soil samples may determine whether concentrations of specific pollutants exceed established action levels, or if the concentrations of pollutants present a risk to public health, welfare, or the environment.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the actual procedures used should be documented and described in an appropriate site report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Soil samples may be collected using a variety of methods and equipment depending on the depth of the desired sample, the type of sample required (disturbed vs. undisturbed), and the soil type. Near-surface soils may be easily sampled using a spade, trowel, and scoop. Sampling at greater depths may be performed using a hand auger, continuous flight auger, a trier, a split-spoon, or, if required, a backhoe.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Chemical preservation of solids is not generally recommended. Samples should, however, be cooled and protected from sunlight to minimize any potential reaction. The amount of sample to be collected and proper sample container type are discussed in ERT/REAC SOP #2003 Rev. 0.0 08/11/94, *Sample Storage, Preservation and Handling*.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary potential problems associated with soil sampling - cross contamination of samples and improper sample collection. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Improper sample collection can involve using contaminated equipment, disturbance of the matrix resulting in compaction of the sample, or inadequate homogenization of the samples where required, resulting in variable, non-representative results.

5.0 EQUIPMENT

Soil sampling equipment includes the following:

- Maps/plot plan
- Safety equipment, as specified in the site-specific Health and Safety Plan
- Survey equipment or global positioning system (GPS) to locate sampling points
- Tape measure
- Survey stakes or flags
- Camera and film
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan
- Appropriate size sample containers
- Ziplock plastic bags
- Logbook
- Labels
- Chain of Custody records and custody seals
- Field data sheets and sample labels
- Cooler(s)
- Ice
- Vermiculite
- Decontamination supplies/equipment
- Canvas or plastic sheet
- Spade or shovel
- Spatula
- Scoop
- Plastic or stainless steel spoons
- Trowel(s)
- Continuous flight (screw) auger
- Bucket auger
- Post hole auger
- Extension rods
- T-handle
- Sampling trier
- Thin wall tube sampler
- Split spoons
- Vehimeyer soil sampler outfit
  - Tubes
  - Points
  - Drive head
  - Drop hammer
  - Puller jack and grip
- Backhoe

6.0 REAGENTS

Reagents are not used for the preservation of soil samples. Decontamination solutions are specified in ERT/REAC SOP #2006 Rev. 0.0 08/11/94, *Sampling Equipment Decontamination*, and the site specific work plan.

7.0 PROCEDURES

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required.
2. Obtain necessary sampling and monitoring equipment.
3. Decontaminate or pre-clean equipment, and ensure that it is in working order.
4. Prepare schedules and coordinate with staff, client, and regulatory agencies, if appropriate.
5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.
6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors, including extent and nature of contaminant, should be considered when selecting sample location. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. All staked locations should be utility-cleared by the property owner or the On-Scene-Coordinator (OSC) prior to soil sampling; and utility clearance should always be confirmed before beginning work.

7.2 Sample Collection

7.2.1 Surface Soil Samples

Collection of samples from near-surface soil can be accomplished with tools such as spades, shovels, trowels, and scoops. Surface material is removed to the required depth and a stainless steel or plastic scoop is then used to collect the sample.

This method can be used in most soil types but is limited to sampling at or near the ground surface. Accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by the sample team member. A flat, pointed mason trowel to cut a block of the desired soil is helpful when undisturbed profiles are required. Tools plated with chrome or other materials should not be used. Plating is particularly common with garden implements such as potting trowels.

The following procedure is used to collect surface soil samples:

1. Carefully remove the top layer of soil or debris to the desired sample depth with a pre-cleaned spade.

2. Using a pre-cleaned, stainless steel scoop, plastic spoon, or trowel, remove and discard a thin layer of soil from the area which came in contact with the spade.

3. If volatile organic analysis is to be performed, transfer the sample directly into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.2 Sampling at Depth with Augers and Thin Wall Tube Samplers

This system consists of an auger, or a thin-wall tube sampler, a series of extensions, and a "T" handle (Figure 1, Appendix A). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the auger. If a core sample is to be collected, the auger tip is then replaced with a thin wall tube sampler. The system is then lowered down the borehole, and driven into the soil to the completion depth. The system is withdrawn and the core is collected from the thin wall tube sampler.

Several types of augers are available; these include: bucket type, continuous flight (screw), and post-hole augers. Bucket type augers are better for direct sample recovery because they provide a large volume of sample in a short time. When continuous flight augers are used, the sample can be collected directly from the flights. The continuous flight augers are satisfactory when a composite of the complete soil column is desired. Post-hole augers have limited utility for sample collection as they are designed to cut through fibrous, rooted, swampy soil and cannot be used below a depth of approximately three feet.

The following procedure is used for collecting soil samples with the auger:

1. Attach the auger bit to a drill rod extension, and attach the "T" handle to the drill rod.

2. Clear the area to be sampled of any surface debris (e.g., twigs, rocks, litter). It may be advisable to remove the first three to six inches of surface soil for an area approximately six inches in radius around the drilling location.

3. Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents accidental brushing of loose material back down the borehole when removing the auger or adding drill rods. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.

4. After reaching the desired depth, slowly and carefully remove the auger from the hole. When sampling directly from the auger, collect the sample after the auger is removed from the hole and proceed to Step 10.

5. Remove auger tip from the extension rods and replace with a pre-cleaned thin wall tube sampler. Install the proper cutting tip.

6. Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the soil. Do not scrape the borehole sides. Avoid hammering the rods as the vibrations may cause the boring walls to collapse.

7. Remove the tube sampler, and unscrew the drill rods.

8. Remove the cutting tip and the core from the device.

9. Discard the top of the core (approximately 1 inch), as this possibly represents material collected before penetration of the layer of concern. Place the remaining core into the appropriate labeled sample container. Sample homogenization is not required.

10. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly.

    When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the auger bit to the drill and assembly, and follow steps 3 through 11, making sure to decontaminate the auger and tube sampler between samples.

12. Abandon the hole according to applicable state regulations. Generally, shallow holes can simply be backfilled with the removed soil material.

7.2.3 Sampling with a Trier

The system consists of a trier, and a "T" handle. The auger is driven into the soil to be sampled and used to extract a core sample from the appropriate depth.

The following procedure is used to collect soil samples with a sampling trier:

1. Insert the trier (Figure 2, Appendix A) into the material to be sampled at a 0° to 45° angle from horizontal. This orientation minimizes the spillage of sample.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.4 Sampling at Depth with a Split Spoon (Barrel) Sampler

Split spoon sampling is generally used to collect undisturbed soil cores of 18 or 24 inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling. The split spoon is then driven to its sampling depth through the bottom of the augured hole and the core extracted.

When split spoon sampling is performed to gain geologic information, all work should

be performed in accordance with ASTM D1586-98, "Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils".

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe on the bottom and the head piece on top.

2. Place the sampler in a perpendicular position on the sample material.

3. Using a well ring, drive the tube. Do not drive past the bottom of the head piece or compression of the sample will result.

4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth.

5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally. This sampler is typically available in 2 and 3 1/2 inch diameters. A larger barrel may be necessary to obtain the required sample volume.

6. Without disturbing the core, transfer it to appropriate labeled sample container(s) and seal tightly.

7.2.5 Test Pit/Trench Excavation

A backhoe can be used to remove sections of soil, when detailed examination of soil characteristics are required. This is probably the most expensive sampling method because of the relatively high cost of backhoe operation.

The following procedures are used for collecting soil samples from test pits or trenches:

1. Prior to any excavation with a backhoe, it is important to ensure that all sampling locations are clear of overhead and buried utilities.

2. Review the site specific Health & Safety plan and ensure that all safety precautions including appropriate monitoring equipment are installed as required.

3. Using the backhoe, excavate a trench approximately three feet wide and approximately one foot deep below the cleared sampling location. Place excavated soils on plastic sheets. Trenches greater than five feet deep must be sloped or protected by a shoring system, as required by OSHA regulations.

4. A shovel is used to remove a one to two inch layer of soil from the vertical face of the pit where sampling is to be done.

5. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In many instances, samples can be collected directly from the backhoe bucket.

6. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7. Abandon the pit or excavation according to applicable state regulations. Generally, shallow excavations can simply be backfilled with the removed soil material.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITY ASSURANCE/QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration

activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OHSA and corporate health and safety procedures, in addition to the procedures specified in the site specific Health & Safety Plan..

12.0 REFERENCES

Mason, B.J. 1983. Preparation of Soil Sampling Protocol: Technique and Strategies. EPA-600/4-83-020.

Barth, D.S. and B.J. Mason. 1984. Soil Sampling Quality Assurance User's Guide. EPA-600/4-84-043.

U.S. Environmental Protection Agency. 1984 Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA-600/4-84-076.

de Vera, E.R., B.P. Simmons, R.D. Stephen, and D.L. Storm. 1980. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018.

ASTM D 1586-98, ASTM Committee on Standards, Philadelphia, PA.

APPENDIX A
Figures
SOP #2012
February 2000

FIGURE 1. Sampling Augers

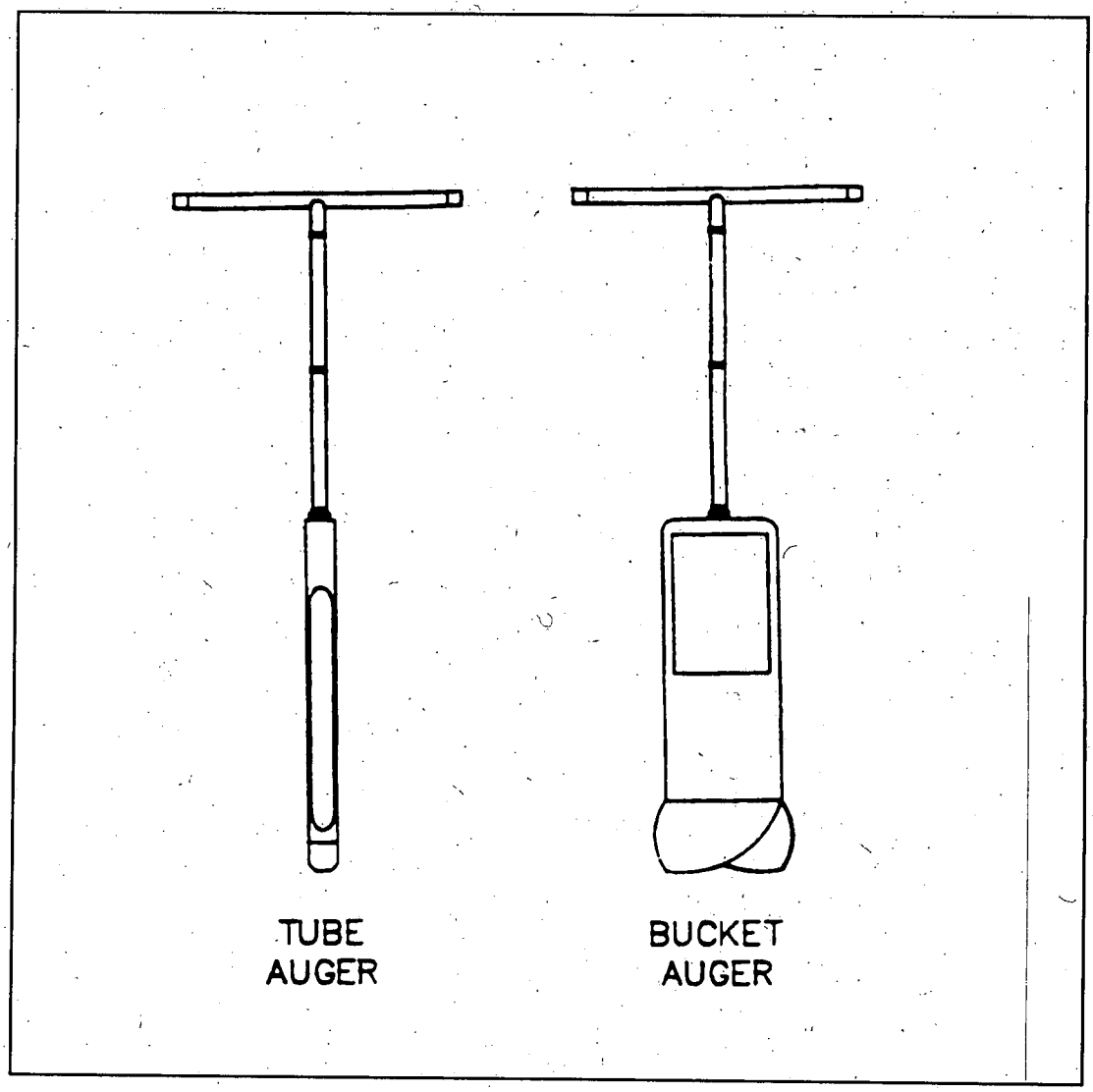
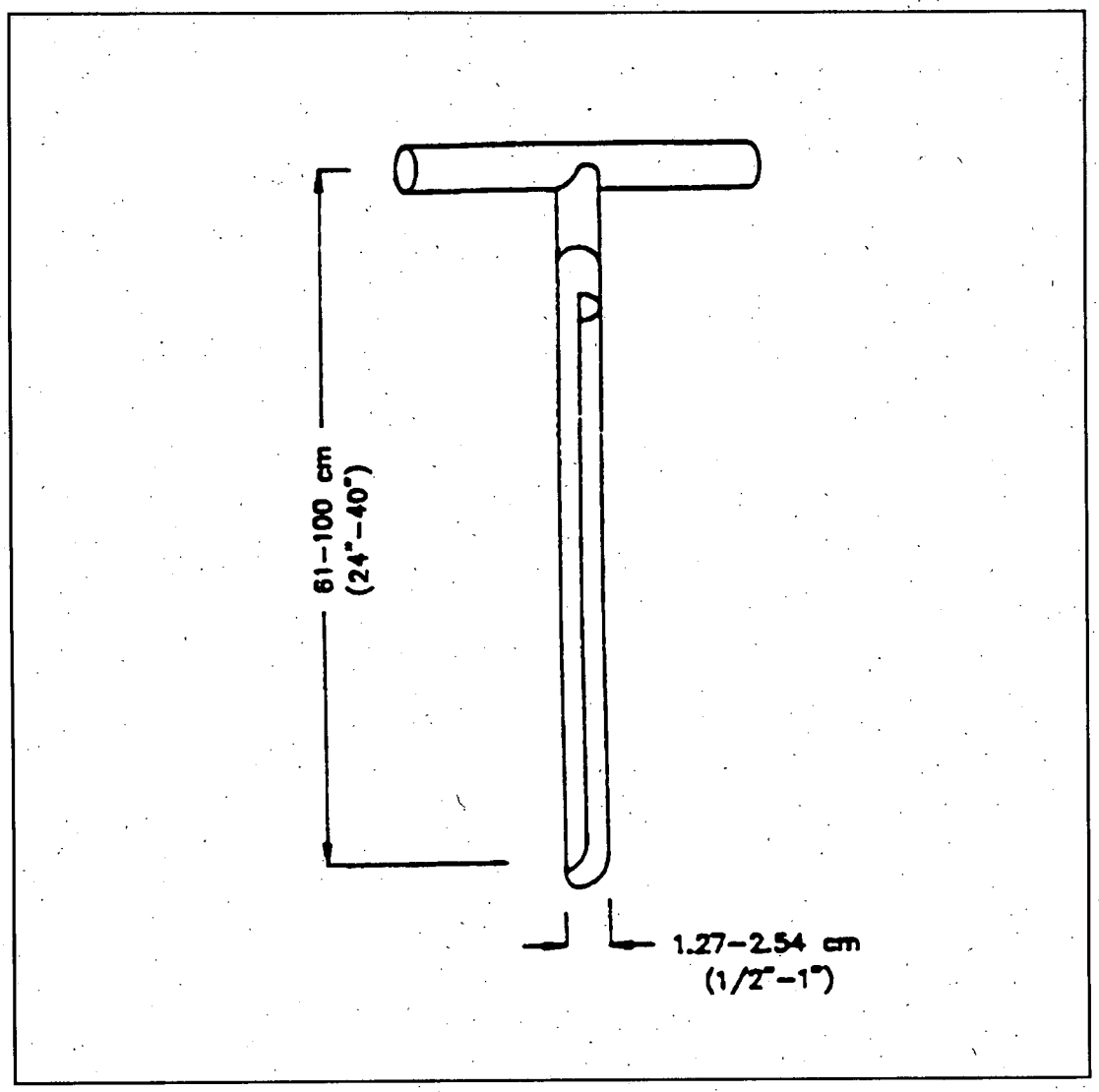


FIGURE 2. Sampling Trier



# SURFACE WATER SAMPLING

SOP#: 2013
DATE: 11/17/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the collection of representative liquid samples, both aqueous and non-aqueous from streams, rivers, lakes, ponds, lagoons, and surface impoundments. It includes samples collected from depth, as well as samples collected from the surface.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Sampling situations vary widely, therefore, no universal sampling procedure can be recommended. However, sampling of both aqueous and non-aqueous liquids from the above mentioned sources is generally accomplished through the use of one of the following samplers or techniques:

- Kemmerer bottle
- Bacon bomb sampler
- Dip sampler
- Direct method

These sampling techniques will allow for the collection of representative samples from the majority of surface waters and impoundments encountered.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Once samples have been collected, the following procedure should be followed:

1. Transfer the sample(s) into suitable, labeled sample containers.
2. Preserve the sample if appropriate, or use pre-preserved sample bottles. Do not overfill bottles if they are pre-preserved.
3. Cap the container, place in a ziploc plastic bag and cool to 4°C.
4. Record all pertinent data in the site logbook and on field data sheets.
5. Complete the Chain of Custody record.
6. Attach custody seals to cooler prior to shipment.
7. Decontaminate all sampling equipment prior to the collection of additional samples with that sampling device.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary interferences or potential problems with surface water sampling. These include cross contamination of samples and improper sample collection.

1. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Refer to the Sampling Equipment Decontamination SOP.

2. Improper sample collection can involve using contaminated equipment, disturbance of the stream or impoundment substrate, and sampling in an obviously disturbed area.

Following proper decontamination procedures and minimizing disturbance of the sample site will eliminate these problems.

## 5.0 EQUIPMENT/APPARATUS

Equipment needed for collection of surface water samples may include (depending on technique chosen):

- Kemmerer bottles
- Bacon bomb sampler
- Dip sampler
- Line and messengers
- Sample bottles/preservatives
- Ziploc bags
- Ice
- Coolers
- Chain of Custody records, custody seals
- Field data sheets
- Decontamination equipment
- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Logbook/waterproof pen
- Sample bottle labels

## 6.0 REAGENTS

Reagents will be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed.

## 7.0 PROCEDURES

### 7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.

2. Obtain the necessary sampling and monitoring equipment.

3. Decontaminate or pre-clean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry, in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. If required the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If collecting sediment samples, this procedure may disturb the bottom.

### 7.2 Representative Sampling Considerations

In order to collect a representative sample, the hydrology and morphometrics of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons, or impoundments, flow patterns in streams, and appropriate sample locations and depths.

Water quality data should be collected in impoundments, and to determine if stratification is present. Measurements of dissolved oxygen, pH, and temperature can indicate if strata exist which would effect analytical results. Measurements should be collected at one-meter intervals from the substrate to the surface using the appropriate instrument (i.e., a Hydrolab or equivalent).

Water quality measurements such as dissolved oxygen, pH, temperature, conductivity, and oxidation-reduction potential can assist in the interpretation of analytical data and the selection of sampling sites and depths when surface water samples are collected.

Generally, the deciding factors in the selection of a sampling device for sampling liquids in streams, rivers, lakes, ponds, lagoons, and surface impoundments are:

1. Will the sample be collected from shore or from a boat?

2. What is the desired depth at which you wish to collect the sample?

3. What is the overall depth and flow direction of river or stream?

4. What type of sample will be collected (i.e., water or lagoon liquids)?

### 7.2.1 Sampler Composition

The appropriate sampling device must be of a proper composition. Selection of samplers constructed of glass, stainless steel, PVC or PFTE (Teflon) should be based upon the analyses to be performed.

## 7.3 Sample Collection

### 7.3.1 Kemmerer Bottle

A Kemmerer bottle (Figure 1, Appendix A) may be used in most situations where site access is from a boat or structure such as a bridge or pier, and where samples at depth are required. Sampling procedures are as follows:

1. Use a properly decontaminated Kemmerer bottle. Set the sampling device so that the sampling end pieces (upper and lower stoppers) are pulled away from the sampling tube (body), allowing the substance to be sampled to pass through this tube.

2. Lower the pre-set sampling device to the predetermined depth. Avoid bottom disturbance.

3. When the Kemmerer bottle is at the required depth, send down the messenger, closing the sampling device.

4. Retrieve the sampler and discharge from the bottom drain the first 10-20 mL to clear any potential contamination of the valve. Transfer the sample to the appropriate sample container.

### 7.3.2 Bacon Bomb Sampler

A bacon bomb sampler (Figure 2, Appendix A) may be used in situations similar to those outlined for the Kemmerer bottle. Sampling procedures are as follows:

1. Lower the bacon bomb sampler carefully to the desired depth, allowing the line for the trigger to remain slack at all times. When the desired depth is reached, pull the trigger line until taut. This will allow the sampler to fill.

2. Release the trigger line and retrieve the sampler.

3. Transfer the sample to the appropriate sample container by pulling up on the trigger.

### 7.3.3 Dip Sampler

A dip sampler (Figure 3, Appendix A) is useful in situations where a sample is to be recovered from an outfall pipe or along a lagoon bank where direct access is limited. The long handle on such a device allows access from a discrete location. Sampling procedures are as follows:

1. Assemble the device in accordance with the manufacturer's instructions.

2. Extend the device to the sample location and collect the sample by dipping the sampler into the substance.

3. Retrieve the sampler and transfer the sample to the appropriate sample container.

### 7.3.4 Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect water samples from the surface directly into the sample bottle. This method is not to be used for sampling lagoons or other impoundments where contact with contaminants is a concern.

Using adequate protective clothing, access the sampling station by appropriate means. For shallow stream stations, collect the sample under the water surface while pointing the sample container upstream; the container must be upstream of the collector. Avoid disturbing the substrate. For lakes and other impoundments, collect the sample under the water surface avoiding surface debris and the boat wake.

When using the direct method, do not use pre-preserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA and corporate health and safety procedures.

More specifically, when sampling lagoons or surface impoundments containing known or suspected hazardous substances, adequate precautions must be taken to ensure the safety of sampling personnel. The sampling team member collecting the sample should not get too close to the edge of the impoundment, where bank failure may cause him/her to lose his/her balance. The person performing the sampling should be on a lifeline and be wearing adequate protective equipment. When conducting sampling from a boat in an impoundment or flowing waters, appropriate boating safety procedures should be followed.

## 12.0 REFERENCES

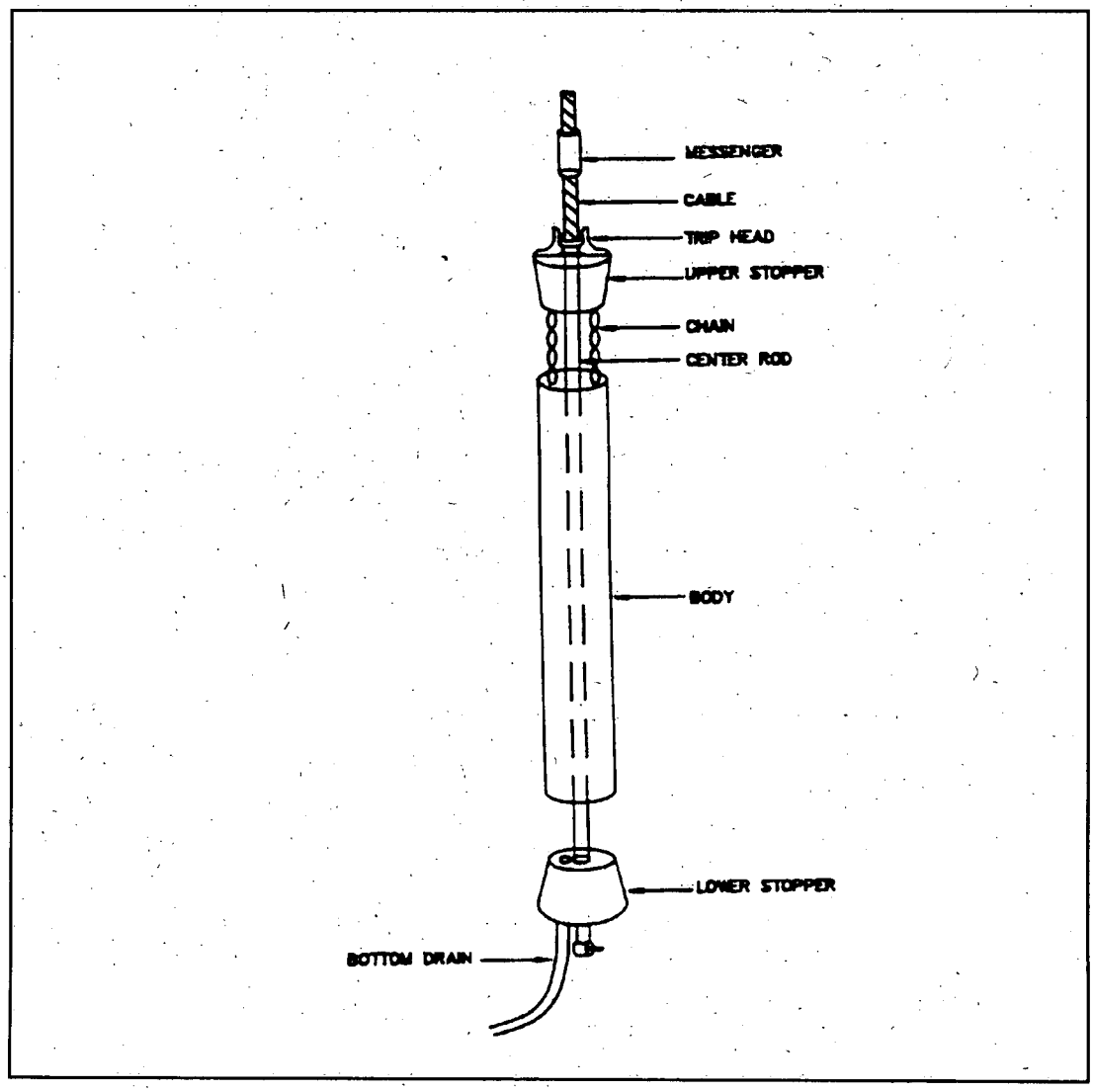
U.S. Geological Survey. 1977. National Handbook or Recommended Methods for Water Data Acquisition. Office of Water Data Coordination Reston, Virginia. (Chapter Updates available).

U.S. Environmental Protection Agency. 1984. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II: Available Sampling Methods, Second Edition. EPA/600/4-84-076.

# APPENDIX A

Figures

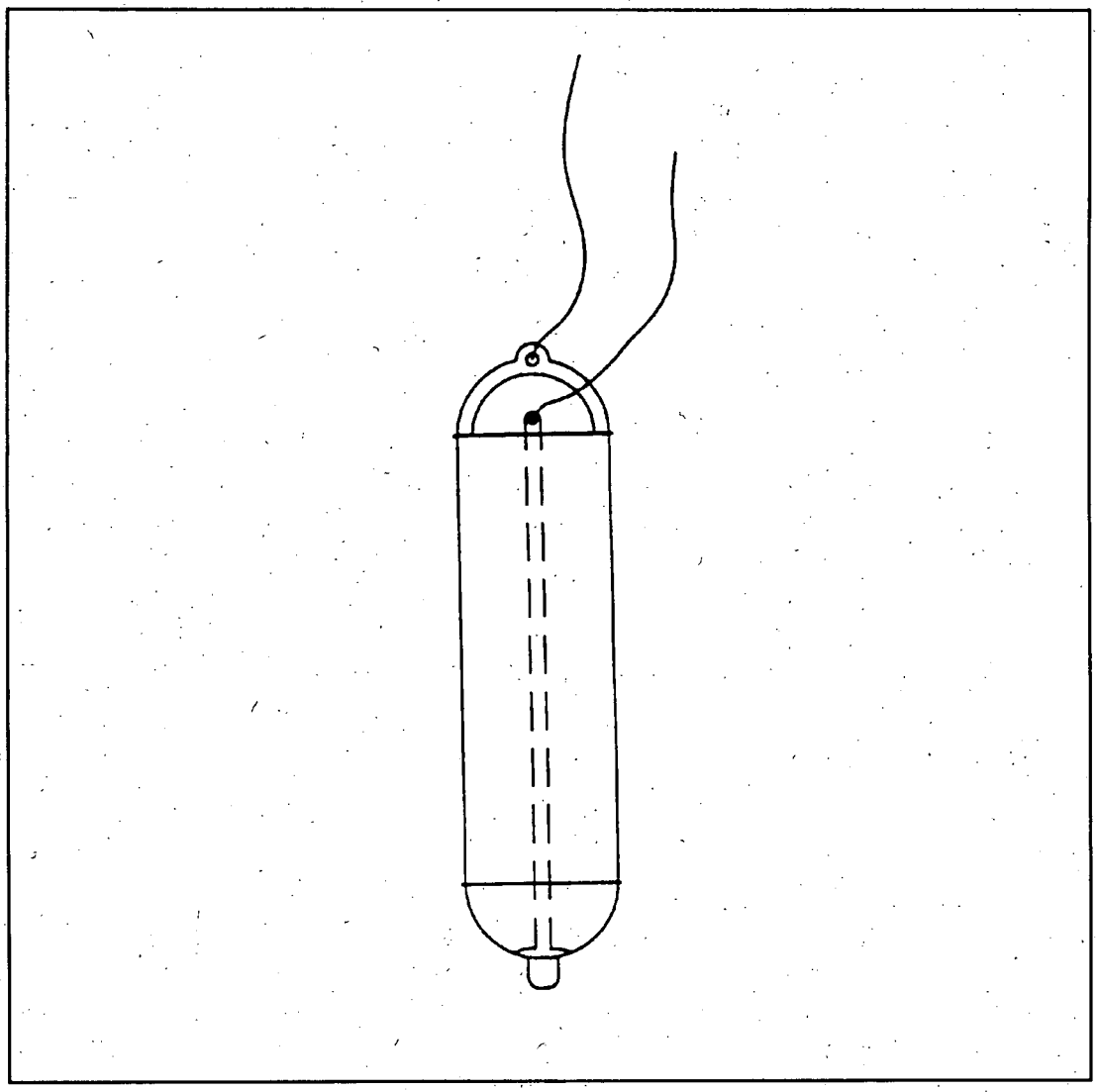
FIGURE 1. Kemmerer Bottle



## APPENDIX A (Cont'd)

Figures

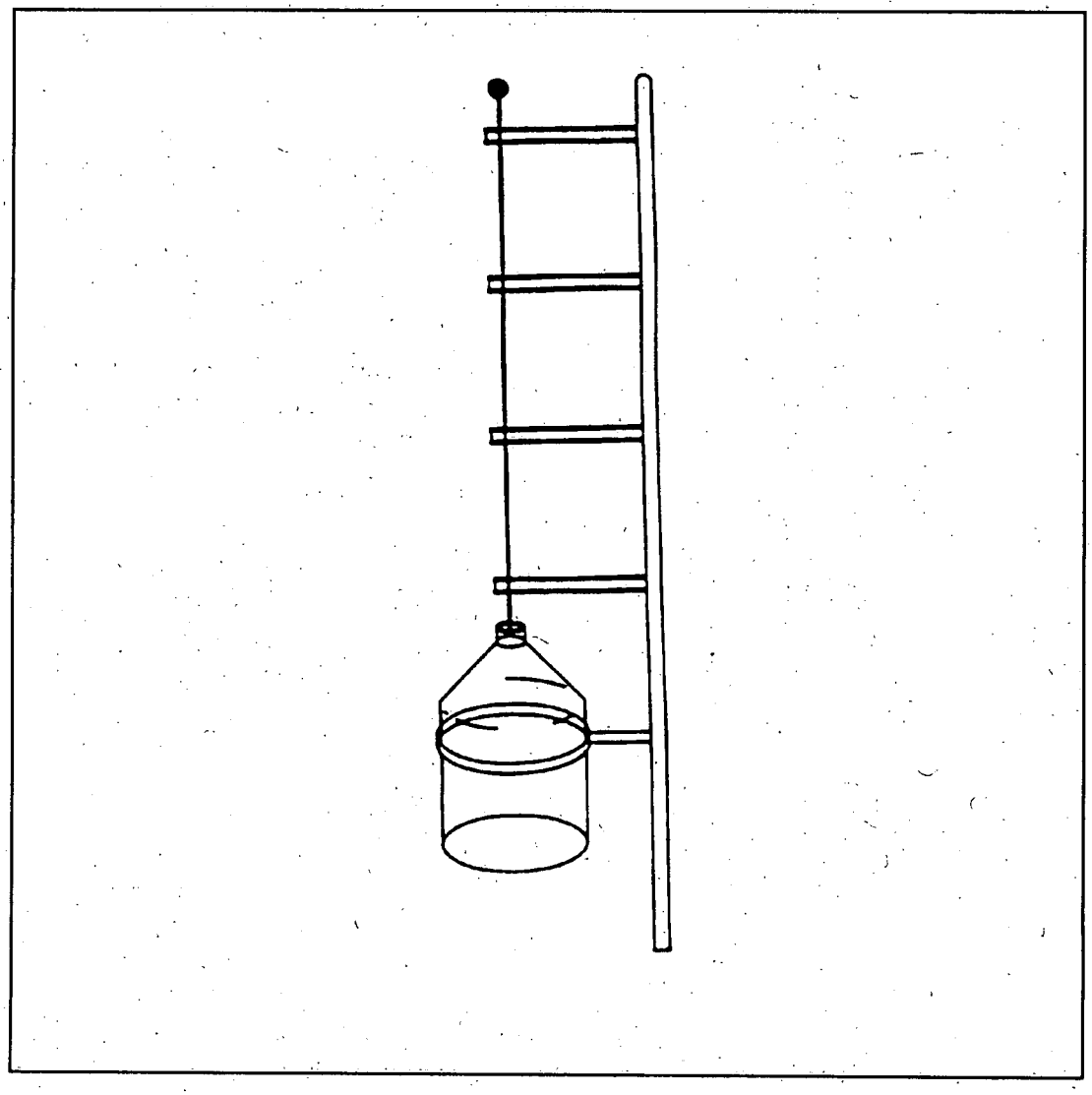
FIGURE 2. Bacon Bomb Sampler



## APPENDIX A (Cont'd)

Figures

FIGURE 3. Dip Sampler



# SEDIMENT SAMPLING

## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the collection of representative sediment samples. Analysis of sediment may be biological, chemical, or physical in nature and may be used to determine the following:

- toxicity;
- biological availability and effects of contaminants;
- benthic biota;
- extent and magnitude of contamination;
- contaminant migration pathways and source;
- fate of contaminants;
- grain size distribution.

The methodologies discussed in this SOP are applicable to the sampling of sediment in both flowing and standing water. They are generic in nature and may be modified in whole or part to meet the handling and analytical requirements of the contaminants of concern, as well as the constraints presented by site conditions and equipment limitations. However, if modifications occur, they should be documented in a site or personal logbook and discussed in reports summarizing field activities and analytical results.

For the purposes of this procedure, sediments are those mineral and organic materials situated beneath an aqueous layer. The aqueous layer may be either static, as in lakes, ponds, and impoundments; or flowing, as in rivers and streams.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Sediment samples may be collected using a variety of methods and equipment, depending on the depth of the aqueous layer, the portion of the sediment profile required (surface vs. subsurface), the type of sample required (disturbed vs. undisturbed), contaminants present, and sediment type.

Sediment is collected from beneath an aqueous layer either directly, using a hand held device such as a shovel, trowel, or auger; or indirectly, using a remotely activated device such as an Ekman or Ponar dredge. Following collection, sediment is transferred from the sampling device to a sample container of appropriate size and construction for the analyses requested. If composite sampling techniques are employed, multiple grabs are placed into a container constructed of inert material, homogenized, and transferred to sample containers appropriate for the analyses requested. The homogenization procedure should not be used if sample analysis includes volatile organics; in this case, sediment, or multiple grabs of sediment, should be transferred directly from the sample collection device or homogenization container to the sample container.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

1. Chemical preservation of solids is generally not recommended. Cooling to 4°C is usually the best approach, supplemented by the appropriate holding time for the analyses requested.

2. Wide mouth glass containers with Teflon lined caps are utilized for sediment samples. The sample volume is a function of the analytical requirements and will be specified in the Work Plan.

3. If analysis of sediment from a discrete depth or location is desired, sediment is transferred directly from the sampling device to a labeled sample container(s) of appropriate size and construction for the analyses

requested. Transfer is accomplished with a stainless steel or plastic lab spoon or equivalent.

4. If composite sampling techniques or multiple grabs are employed, equal portions of sediment from each location are deposited into a stainless steel, plastic, or other appropriate composition (e.g., Teflon) containers. The sediment is homogenized thoroughly to obtain a composite representative of the area sampled. The composite sediment sample is transferred to a labeled container(s) of appropriate size and construction for the analyses requested. Transfer of sediment is accomplished with a stainless steel or plastic lab spoon or equivalent. Samples for volatile organic analysis must be transferred directly from the sample collection device or pooled from multiple areas in the homogenization container prior to mixing. This is done to minimize loss of contaminant due to volatilization during homogenization.

5. All sampling devices should be decontaminated, then wrapped in aluminum foil. The sampling device should remain in this wrapping until it is needed. Each sampling device should be used for only one sample. Disposable sampling devices for sediment are generally impractical due to cost and the large number of sediment samples which may be required. Sampling devices should be cleaned in the field using the decontamination procedure described in the Sampling Equipment Decontamination SOP.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Substrate particle size and organic matter content are a direct consequence of the flow characteristics of a waterbody. Contaminants are more likely to be concentrated in sediments typified by fine particle size and a high organic matter content. This type of sediment is most likely to be collected from depositional zones. In contrast, coarse sediments with low organic matter content do not typically concentrate pollutants and are generally found in erosional zones. The selection of a sampling location can, therefore, greatly influence the analytical results and should be justified and specified in the Work Plan.

## 5.0 EQUIPMENT/APPARATUS

Equipment needed for collection of sediment samples may include:

- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Stainless steel, plastic, or other appropriate composition bucket
- 4-oz., 8-oz., and one-quart wide mouth jars w/Teflon lined lids
- Ziploc plastic bags
- Logbook
- Sample jar labels
- Chain of Custody records, field data sheets
- Cooler(s)
- Ice
- Decontamination supplies/equipment
- Spade or shovel
- Spatula
- Scoop
- Trowel
- Bucket auger
- Tube auger
- Extension rods
- "T" handle
- Sediment coring device (tube, drive head, eggshell check value, nosecone, acetate tube, extension rods, "T" handle)
- Ponar dredge
- Ekman dredge
- Nylon rope or steel cable
- Messenger device

## 6.0 REAGENTS

Reagents are not used for preservation of sediment samples. Decontamination solutions are specified in the Sampling Equipment Decontamination SOP.

## 7.0 PROCEDURES

### 7.1 Preparation

1. Determine the objective(s) and extent of the sampling effort. The sampling methods to be employed, and the types and amounts of equipment and supplies required will be a function of site characteristics and objectives of the study.

2. Obtain the necessary sampling and monitoring equipment.

3. Prepare schedules, and coordinate with staff, client, and regulatory agencies, if appropriate.

4. Decontaminate or preclean equipment, and ensure that it is in working order.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors including flow regime, basin morphometry, sediment characteristics, depth of overlying aqueous layer, contaminant source, and extent and nature of contamination should be considered when selecting sample locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

### 7.2 Sample Collection

Selection of a sampling device is most often contingent upon: (1) the depth of water at the sampling location, and (2) the physical characteristics of the sediment to be sampled. The following procedures may be utilized:

#### 7.2.1 Sampling Surface Sediment with a Trowel or Scoop from Beneath a Shallow Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth and a shallow aqueous layer is considered to range from 0 to 12 inches in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with tools such as spades, shovels, trowels, and scoops. Although this method can be used to collect both unconsolidated/consolidated sediment, it is limited somewhat by the depth and movement of the aqueous layer. Deep and rapidly flowing water render this method less accurate than others discussed below. However, representative samples can be collected with this procedure in shallow sluggish water provided care is demonstrated by the sample team member. A stainless steel or plastic sampling implement will suffice in most applications. Care should be exercised to avoid the use of devices plated with chrome or other materials; plating is particularly common with garden trowels.

The following procedure will be used to collect sediment with a scoop, shovel, or trowel:

1. Using a decontaminated sampling implement, remove the desired thickness and volume of sediment from the sampling area.

2. Transfer the sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

3. Surface water should be decanted from the sample or homogenization container prior to sealing or transfer; care should be taken to retain the fine sediment fraction during this procedure.

#### 7.2.2 Sampling Surface Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of bucket auger or tube auger, a series of extensions, and a "T" handle (Figure 1, Appendix A). The use of additional extensions in conjunction with a bucket auger can increase the depth of water from which sediment can be collected from 24 inches to 10 feet or more. However, sample handling and manipulation increases

in difficulty with increasing depth of water. The bucket auger or tube auger is driven into the sediment and used to extract a core. The various depths represented by the core are homogenized or a subsample of the core is taken from the appropriate depth.

The following procedure will be used to collect sediment samples with a bucket auger or tube auger:

1. An acetate core may be inserted into the bucket auger or tube auger prior to sampling if characteristics of the sediments or waterbody warrant. By using this technique, an intact core can be extracted.

2. Attach the auger head to the required length of extensions, then attach the "T" handle to the upper extension.

3. Clear the area to be sampled of any surface debris.

4. Insert the bucket auger or tube auger into the sediment at a 0° to 20° angle from vertical. This orientation minimizes spillage of the sample from the sampler upon extraction from the sediment and water.

5. Rotate the auger to cut a core of sediment.

6. Slowly withdraw the auger; if using a tube auger, make sure that the slot is facing upward.

7. Transfer the sample or a specified aliquot of sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

### 7.2.3 Sampling Deep Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer

For the purpose of this method, deep sediment is considered to range from six to greater than 18 inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches. Collection of deep sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a bucket auger, a tube auger, a series of extensions and a "T" handle. The use of additional extensions can increase the depth of water from which sediment can be collected from 24 inches to five feet or more. However, water clarity must be high enough to permit the sampler to directly observe the sampling operation. In addition, sample handling and manipulation increases in difficulty with increasing depth of water. The bucket auger is used to bore a hole to the upper range of the desired sampling depth and then withdrawn. The tube auger is then lowered down the borehole, and driven into the sediment to the lower range of the desired sampling depth. The tube is then withdrawn and the sample recovered from the tube. This method can be used to collect firmly consolidated sediments, but is somewhat limited by the depth of the aqueous layer, and the integrity of the initial borehole.

The following procedure will be used to collect deep sediment samples with a bucket auger and a tube auger:

1. Attach the bucket auger bit to the required lengths of extensions, then attach the "T" handle to the upper extension.

2. Clear the area to be sampled of any surface debris.

3. Begin augering, periodically removing any accumulated sediment (i.e., cuttings) from the auger bucket. Cuttings should be disposed of far enough from the sampling area to minimize cross contamination of various depths.

4. After reaching the upper range of the desired depth, slowly and carefully remove bucket auger from the boring.

5. Attach the tube auger bit to the required lengths of extensions, then attach the "T" handle to the upper extension.

6. Carefully lower tube auger down borehole using care to avoid making contact with the borehole sides and, thus, cross contaminating the sample. Gradually force tube auger into sediment to the lower range of the desired sampling depth. Hammering of the tube auger to facilitate coring should be avoided as the vibrations may cause the boring walls

to collapse.

7. Remove tube auger from the borehole, again taking care to avoid making contact with the borehole sides and, thus, cross contaminating the sample.

8. Discard the top of core (approximately 1 inch); as this represents material collected by the tube auger before penetration to the layer of concern.

9. Transfer sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

### 7.2.4 Sampling Surface Sediment with an Ekman or Ponar Dredge from Beneath a Shallow or Deep Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth. Collection of surface sediment can be accomplished with a system consisting of a remotely activated device (dredge) and a deployment system. This technique consists of lowering a sampling device (dredge) to the surface of the sediment by use of a rope, cable, or extended handle. The mechanism is activated, and the device entraps sediment in spring loaded or lever operated jaws.

An Ekman dredge is a lightweight sediment sampling device with spring activated jaws. It is used to collect moderately consolidated, fine textured sediment. The following procedure will be used for collecting sediment with an Ekman dredge (Figure 2, Appendix A):

1. Attach a sturdy nylon rope or stainless steel cable through the hole on the top of the bracket, or secure the extension handle to the bracket with machine bolts.

2. Attach springs to both sides of the jaws. Fix the jaws so that they are in open position by placing trip cables over the release studs. Ensure that the hinged doors on the dredge top are free to open.

3. Lower the sampler to a point 4 to 6 inches above the sediment surface.

4. Drop the sampler to the sediment.

5. Trigger the jaw release mechanism by lowering a messenger down the line, or by depressing the button on the upper end of the extension handle.

6. Raise the sampler and slowly decant any free liquid through the top of the sampler. Care should be taken to retain the fine sediment fraction during this procedure.

7. Open the dredge jaws and transfer the sample into a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment grabs until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

A Ponar dredge is a heavyweight sediment sampling device with weighted jaws that are lever or spring activated. It is used to collect consolidated fine to coarse textured sediment. The following procedure will be used for collecting sediment with a Ponar dredge (Figure 3, Appendix A):

1. Attach a sturdy nylon rope or steel cable to the ring provided on top of the dredge.

2. Arrange the Ponar dredge with the jaws in the open position, setting the trip bar so the sampler remains open when lifted from the top. If the dredge is so equipped, place the spring loaded pin into the aligned holes in the trip bar.

3. Slowly lower the sampler to a point approximately two inches above the sediment.

4. Drop the sampler to the sediment. Slack on

the line will release the trip bar or spring loaded pin; pull up sharply on the line closing the dredge.

5. Raise the dredge to the surface and slowly decant any free liquid through the screens on top of the dredge. Care should be taken to retain the fine sediment fraction during this operation.

6. Open the dredge and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenized and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

### 7.2.5 Sampling Subsurface Sediment with a Coring Device from Beneath a Shallow Aqueous Layer

For purposes of this method, subsurface sediment is considered to range from 6 to 24 inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches in depth. Collection of subsurface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a tube sampler, acetate tube, eggshell check valve, nosecone, extensions, and "T" handle, or drivehead. The use of additional extensions can increase the depth of water from which sediment can be collected from 24 inches to 10 feet or more. This sampler may be used with either a drive hammer for firm sediment, or a "T" handle for soft sediment. However, sample handling and manipulation increases in difficulty with increasing depth of water.

The following procedure describes the use of a sample coring device (Figure 4, Appendix A) used to collect subsurface sediments.

1. Assemble the coring device by inserting the acetate core into the sampling tube.

2. Insert the "egg shell" check valve into the lower end of the sampling tube with the convex surface positioned inside the acetate core.

3. Screw the nosecone onto the lower end of the sampling tube, securing the acetate tube and eggshell check valve.

4. Screw the handle onto the upper end of the sampling tube and add extension rods as needed.

5. Place the sampler in a perpendicular position on the sediment to be sampled.

6. If the "T" handle is used, place downward pressure on the device until the desired depth is reached. After the desired depth is reached, rotate the sampler to shear off the core at the bottom. Slowly withdraw the sampler from the sediment and proceed to Step 15.

7. If the drive hammer is selected, insert the tapered handle (drive head) of the drive hammer through the drive head.

8. Drive the sampler into the sediment to the desired depth.

9. Record the length of the tube that penetrated the sample material, and the number of blows required to obtain this depth.

10. Remove the drive hammer and fit the keyhole-like opening on the flat side of the hammer onto the drive head. In this position, the hammer serves as a handle for the sampler.

11. Rotate the sampler to shear off the core at the bottom.

12. Lower the sampler handle (hammer) until it just clears the two ear-like protrusions on the drive head, and rotate about 90°.

13. Slowly withdraw the sampler from the sediment. If the drivehead was used, pull the hammer upwards and dislodge the sampler from the sediment.

14. Carefully remove the coring device from the water.

15. Unscrew the nosecone and remove the eggshell check valve.

16. Slide the acetate core out of the sampler tube. Decant surface water, using care to retain the fine sediment fraction. If head space is present in the upper end, a hacksaw may be used to shear the acetate tube off at the sediment surface. The acetate core may then be capped at both ends. Indicate on the acetate tube the appropriate orientation of the sediment core using a waterproof marker. The sample may be used in this fashion, or the contents transferred to a sample or homogenization container.

17. Open the acetate tube and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA/OSHA and Corporate health and safety procedures.

More specifically, when sampling sediment from waterbodies, physical hazards must be identified and adequate precautions must be taken to ensure the safety of the sampling team. The team member collecting the sample should not get too close to the edge of the waterbody, where bank failure may cause loss of balance. To prevent this, the person performing the sampling should be on a lifeline, and be wearing adequate protective equipment. If sampling from a vessel is determined to be necessary, appropriate protective measures must be implemented.

## 12.0 REFERENCES

Mason, B.J., Preparation of Soil Sampling Protocol: Technique and Strategies. 1983 EPA-600/4-83-020.

Barth, D.S. and B.J. Mason, Soil Sampling Quality Assurance User's Guide. 1984 EPA-600/4-84-043.

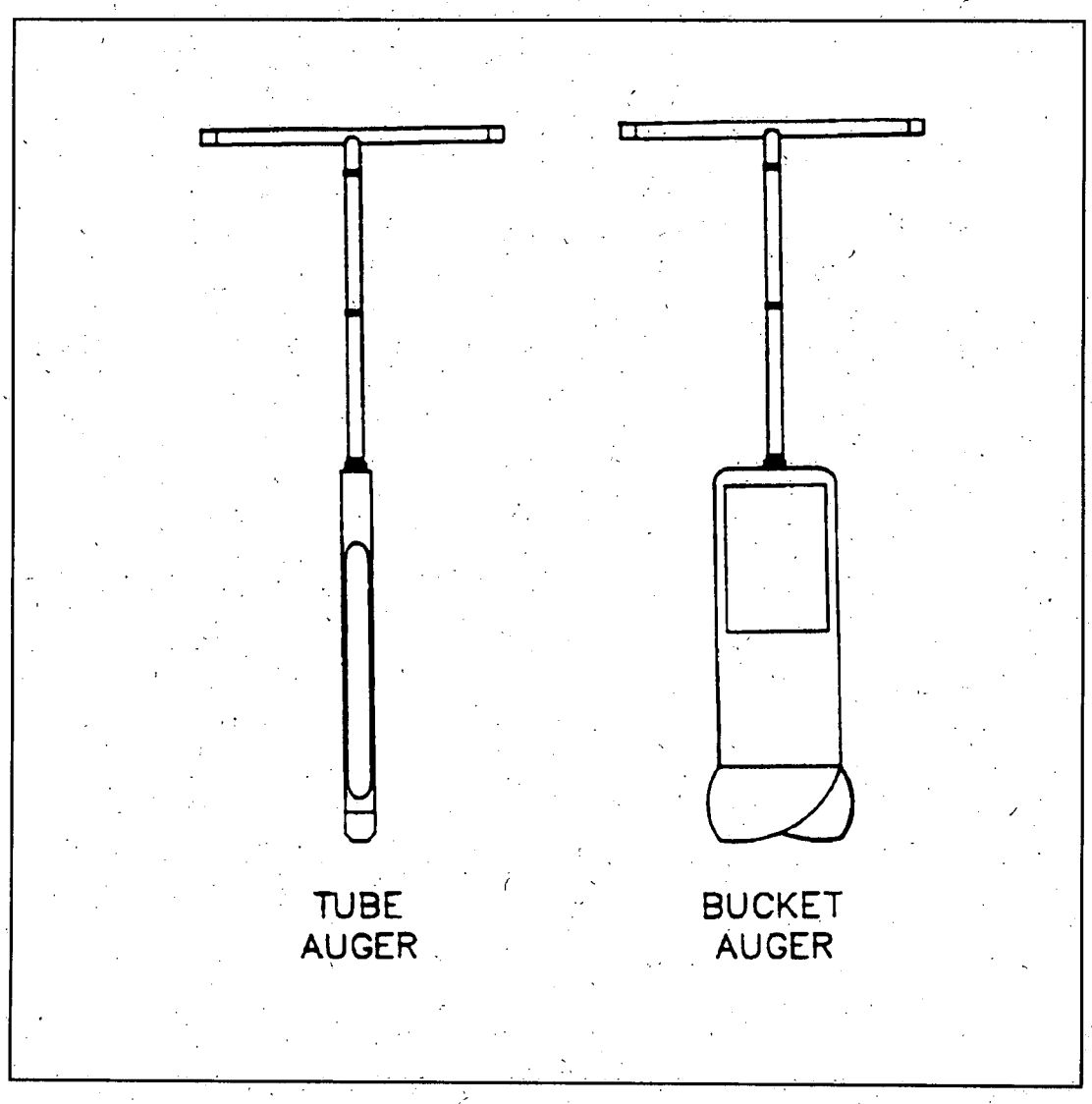
U.S. EPA. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. 1984 EPA-600/4-84-076.

de Vera, E.R., B.P. Simmons, R.D. Stephen, and D.L. Storm. Samplers and Sampling Procedures for Hazardous Waste Streams. 1980 EPA-600/2-80-018.

## APPENDIX A

Figures

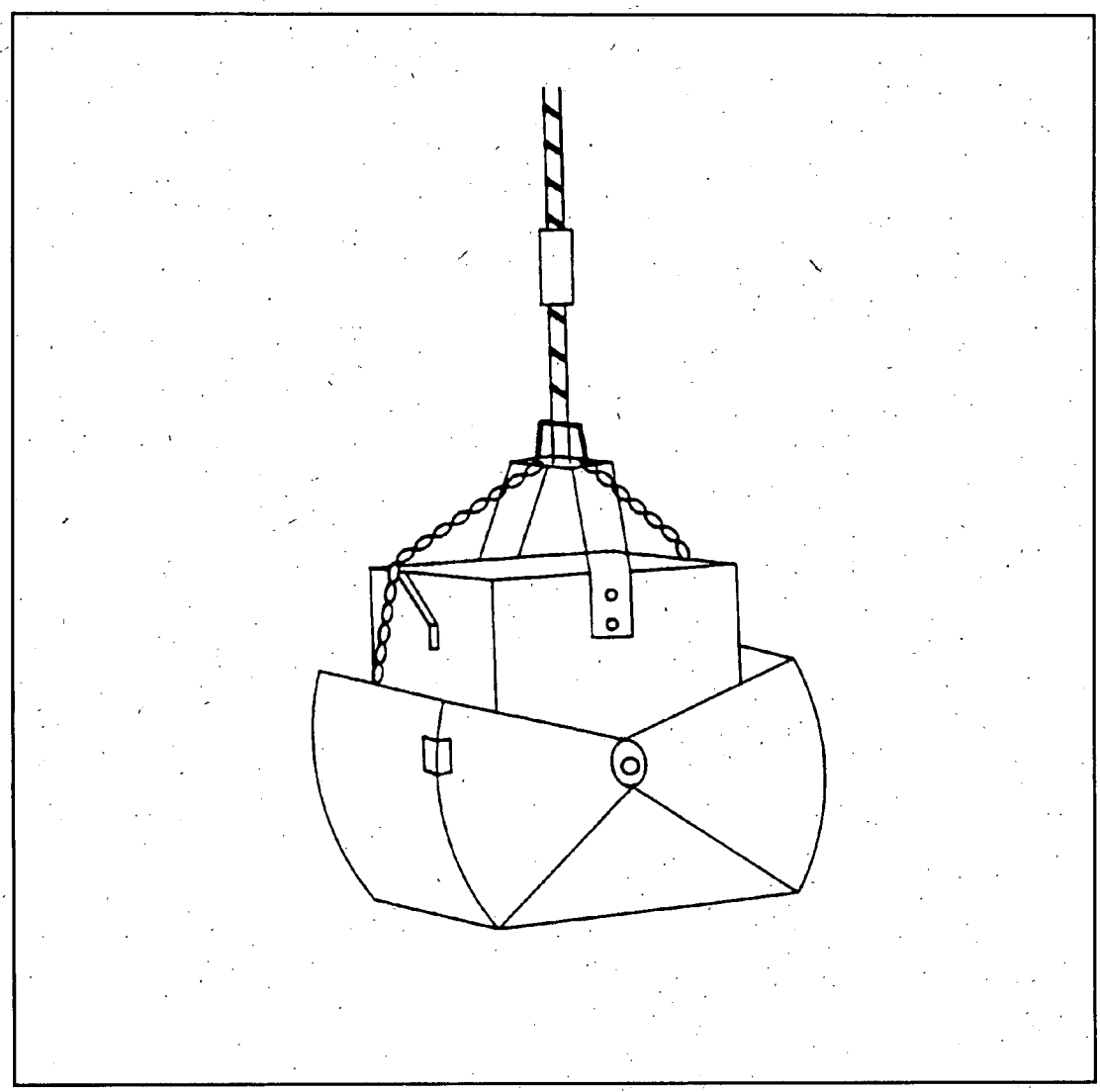
FIGURE 1. Sampling Auger



## APPENDIX A (Cont'd)

Figures

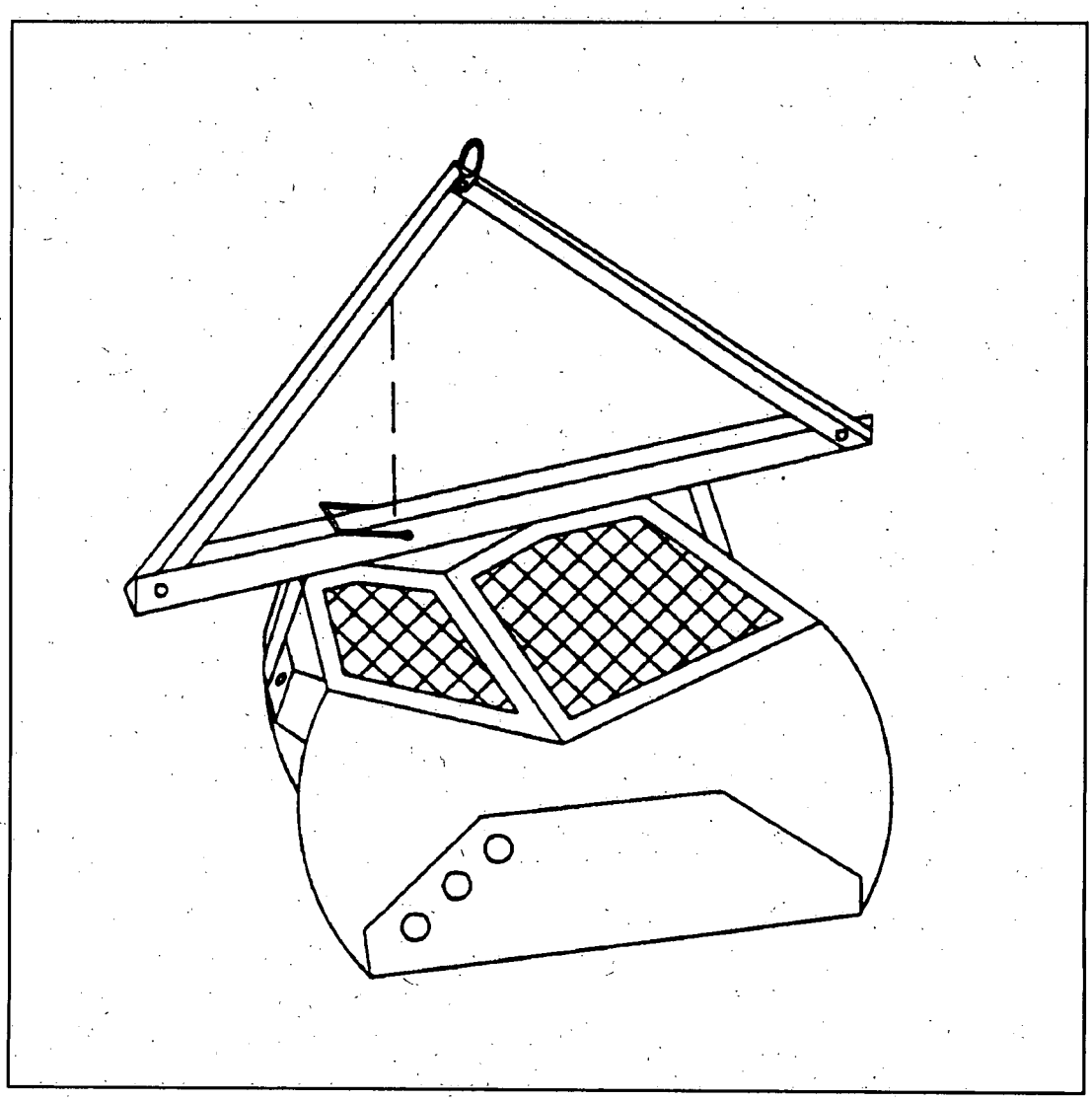
FIGURE 2. Ekman Dredge



## APPENDIX A (Cont'd)

Figures

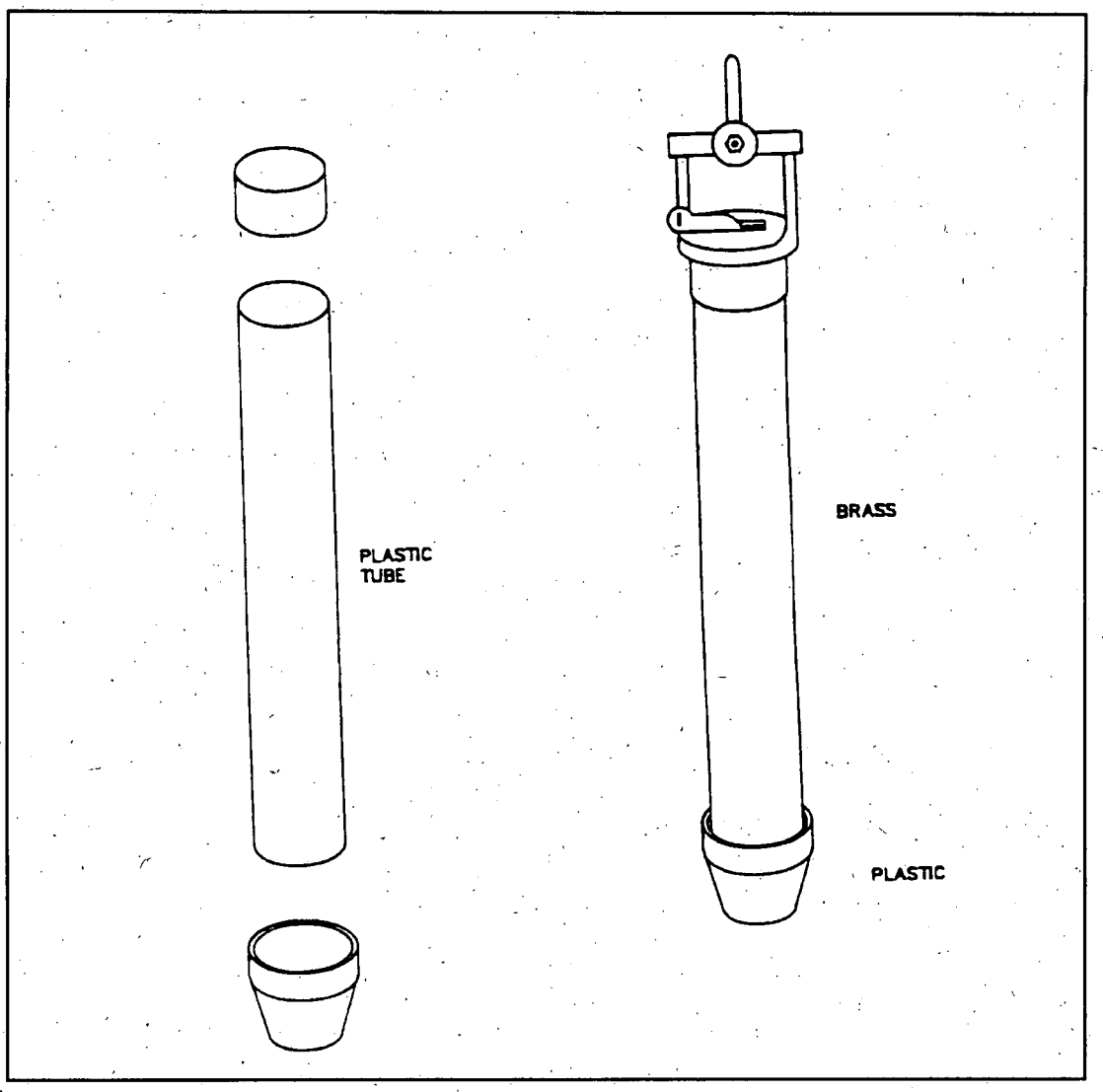
FIGURE 3. Ponar Dredge



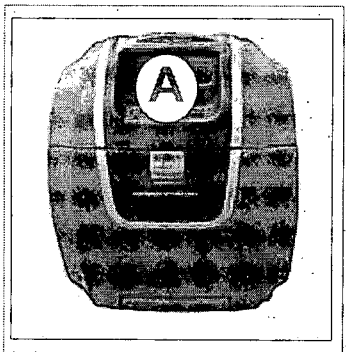
## APPENDIX A (Cont'd)

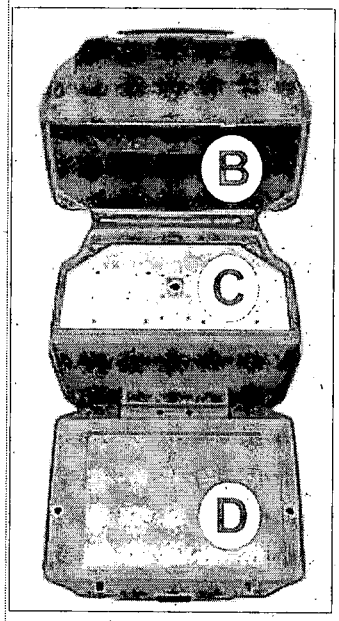
Figures

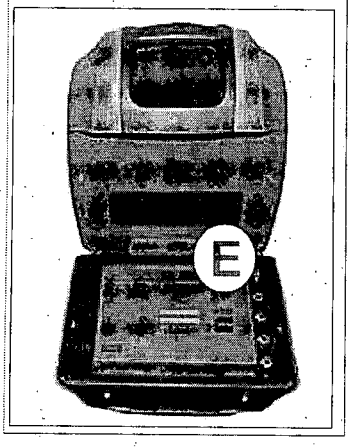
FIGURE 4. Sample Coring Device



# 1. Introduction and System Tour



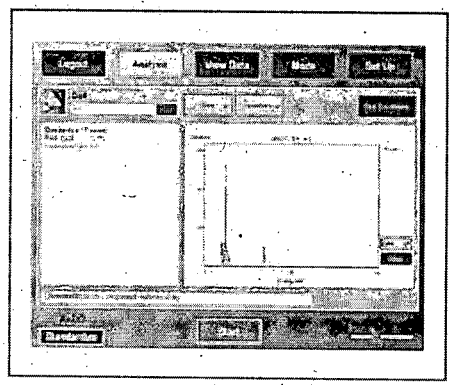

***Getting Started* includes:**

- Tour of the system noting all major components.
- Instructions for these tasks...



## Tour of the *X-50 Mobile XRF* System

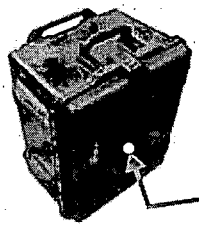
A. **Molded enclosure** that forms a portable, radiation-safe test chamber.
B. **Hinged lid** with safety interlocks to ensure a closed beam system. Handle contains high intensity safety indicator lights.
C. **Main chassis** with test platform and Kapton measurement window.
   - Chassis also contains sub-systems for...
     - Excitation including multibeam capability
     - Detection
     - Safety Interlocks
     - Input/Output (I/O) Panel
D. **Computer**, industrial style, including:
   - A completely integrated package featuring...
     - Licensed Windows® XP Embedded Runtime software.
     - Folding panel with touch-screen I/O with consolidated keyboard function.
E. **Application Software**
   - Easy operations with InnovX Version 2.0 User Interface
   - Extensive sample identification and analysis.
   - Fast results that can be viewed or saved.
   - Major modes include...
     - Soil (multibeam options)
     - Mining
     - Analytical



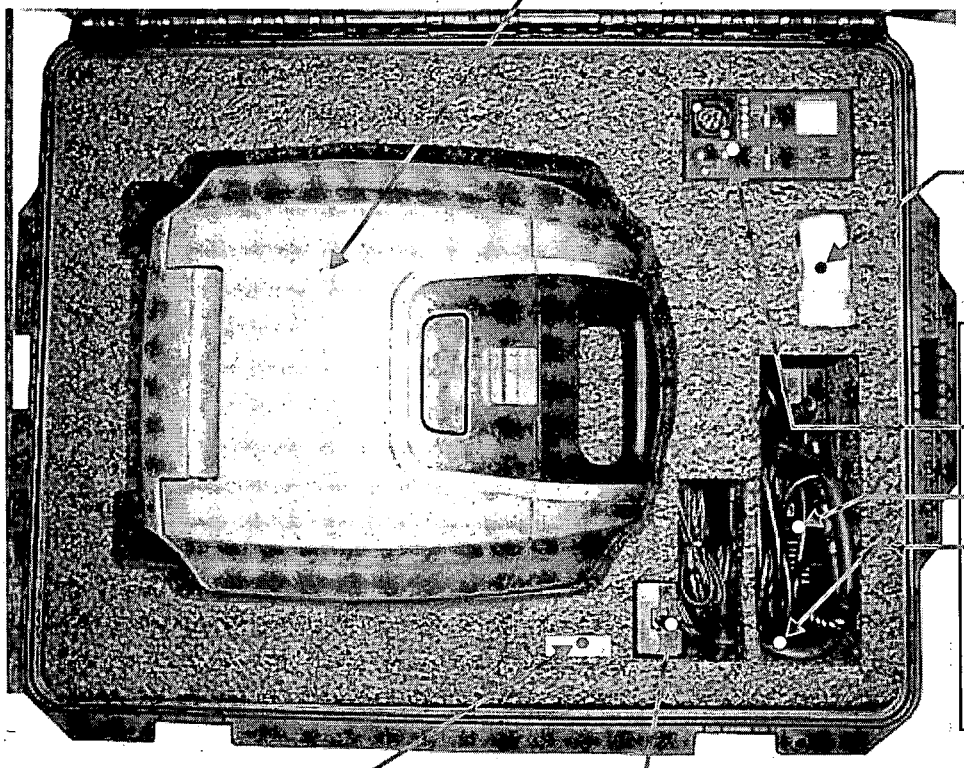
# 2. Unpack the Instrument

The X-50 analyzer and its accessories are shipped in an industrial carry case.
Use these steps to unpack the system:

1. Remove carry case from shipping carton.
2. Open the carry case and remove the X-50 instrument and all accessories.
3. Look for obvious damage to the parts.
4. Immediately report any problems to Innov-X.



## ITEM CHECKLIST for Innov-X Systems X-50 Mobile XRF Analyzer



- ❒ Industrial Carry Case
- ❒ X-50 Analyzer
- ❒ Reference Samples
- ❒ Standardization Coupon
- ❒ AC Power Adapter (for X-50)
- ❒ End User Documentation incl. S/W License (not shown)

***Optional Accessories***

- ❒ Li-Ion Battery
- ❒ Battery Charger Assembly
- ❒ Interconnect Cable
- ❒ Sample Holder/Guide (not shown)

# 3. Hardware Setup

When the X-50 is removed from its carrying case it is "ready to run."
**No assembly is required.**
However, there are physical and cabling considerations.

## a. Physical Planning

– Where will the instrument be used?

It weighs about 26 pounds (11 kilograms). It can sit on a lab table (inside) or on the ground (outside at field sites).

– What precautions must be observed for outdoor use?

Do not operate it in the rain.

The unit can be operated when sitting at an angle. If the sample remains stationary over the measurement window and the lid closes properly, the test can proceed.

– How much space (area) to allocate?

To make a minimum footprint, add at least 6 inches beyond the actual 12.5" width. Plan on a 27" span front-to-back when the lid and computer panel are open.

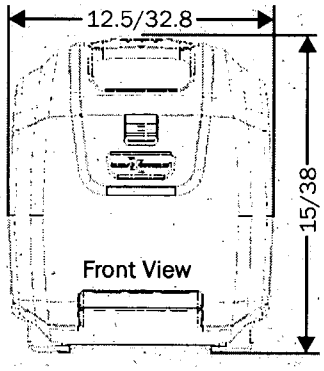
• Ensure that the cooling vents are not obstructed.

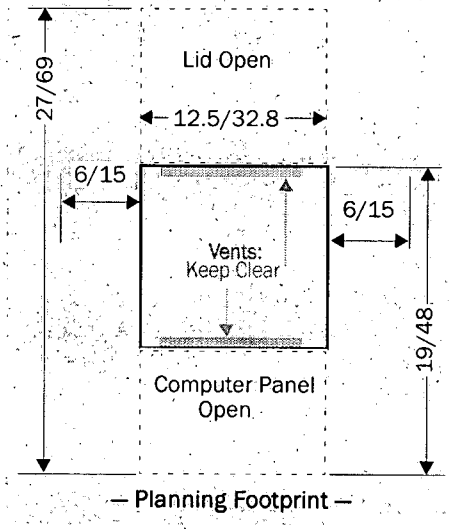
– Any special space issues for height?

The computer/monitor has a touchscreen input. Operator must be able to access the screen comfortably and reliably.

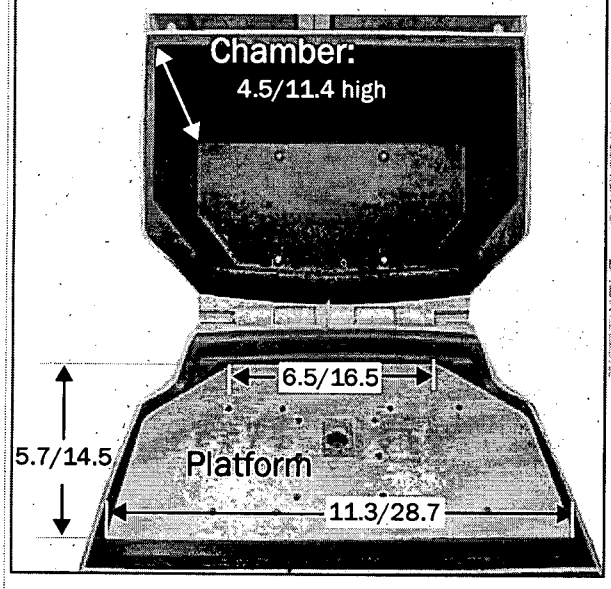
– What are the electrical power requirements?

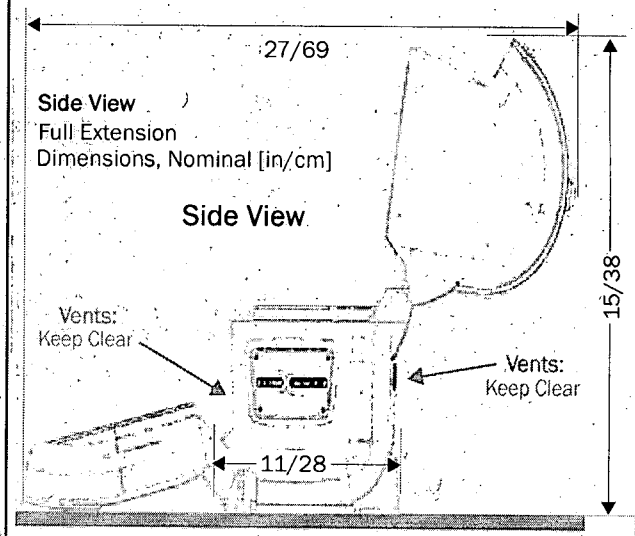
Minimal – Less than 70 watts draw.



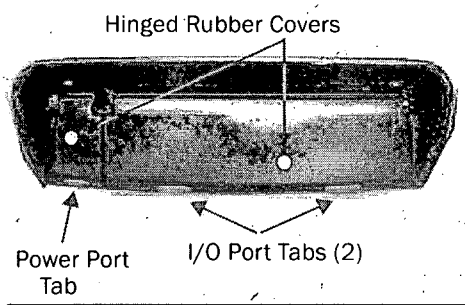




Prior to measuring a sample, note the dimensions of the test chamber/platform.
Ensure that the Lid can close completely



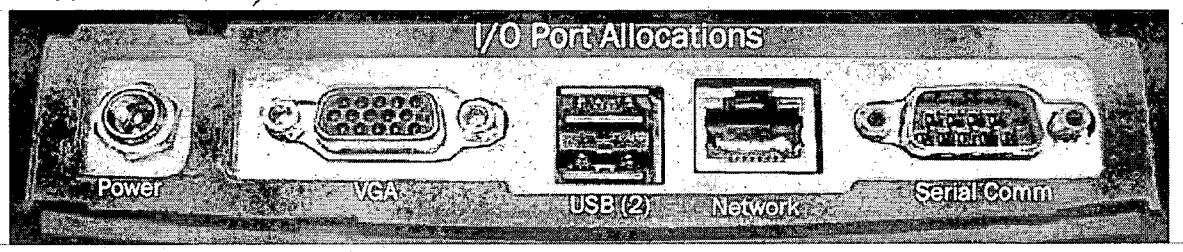



## b. Cable Connections




Lift the hinged rubber covers from the Power port and I/O panel located on the lower rear of the unit to reveal:

- **Power** port for AC Power adapter or Battery cable input.
- **VGA port** to attach an external monitor.
- **USB ports (2)** can be used for...
  - Local data storage via flash memory device.
  - External keyboard
  - External mouse
- **RJ45 socket** for network access (hardwired).
- **Serial Comm** port to attach external devices.



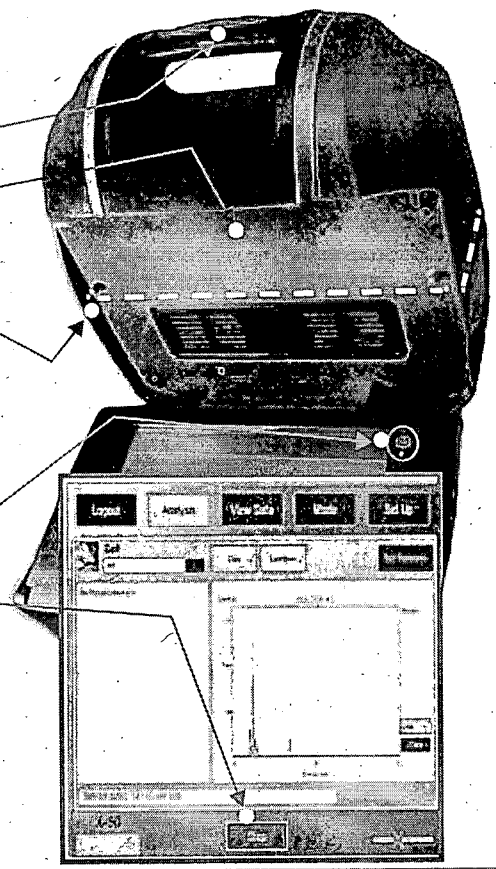

# 4.Safety Features

## a. Hardware

| | |
|---|---|
| X-Ray Indicator Handle | Three high intensity red LEDs glow when the X-ray beam is ON |
| Shielding | Entire test chamber (lid and measurement platform) is shielded. |
| Interlock Sensors | Lid interlocks ensure lid is closed prior to X-rays turning ON. Interrupts beam (X-rays OFF) if lid is lifted during an active test. |

## b. Emergency Shutoff

| | |
|---|---|
| Membrane Switch | Press and hold **I/O** switch; entire unit shuts down within 5 seconds. |
| **STOP** button on User Interface (UI) | Press **STOP** button on UI to terminate X-ray beam immediately. |
| Power Cord | Pull Power adapter cord from unit; entire unit immediately shuts down |

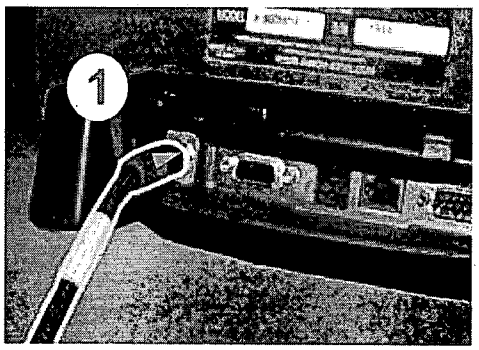


# 5. Operations

## Typical Startup Sequence

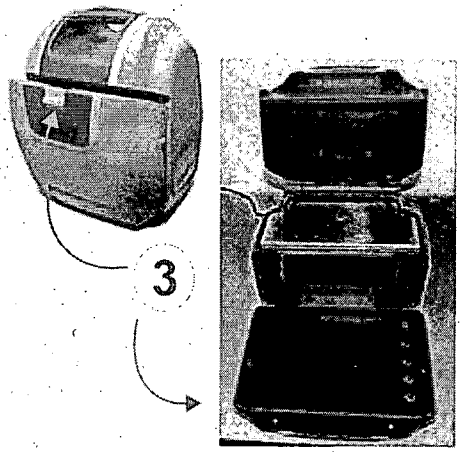
1. Plug in power using the AC adapter or battery.
2. Set up other I/O conditions such as cabling alternatives, memory card, et al, for your needs
3. Pull the blue latch down and gently swing the touchscreen computer panel out and down.

> **TIP** Support the panel on the same horizontal surface (bench or desk) as the main body of the X-50.

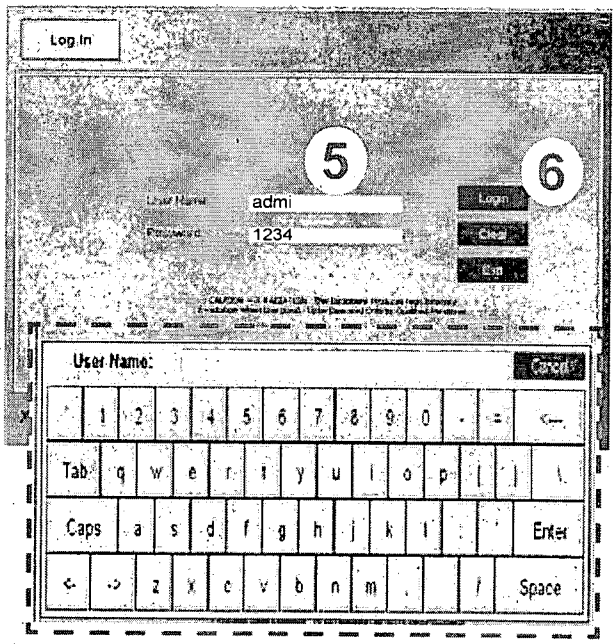


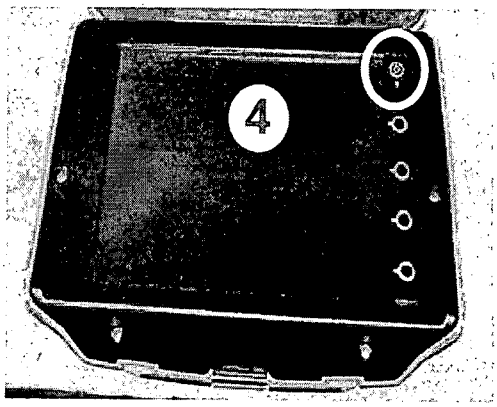

4. Turn on computer with the button (membrane switch) in the upper right corner.
   - Green LED comes on;
   - Windows® XP Embedded Runtime loads;
   - Electronic circuitry (including fans) comes on;
   - The X-50 Version 2.0 User Interface (UI) loads.
5. Enter your *User Name* and *Password*
   Touch each blank field to call the virtual keyboard

> **TIP** The default information is:
> *User Name* --> admi
> *Password* —> 1234

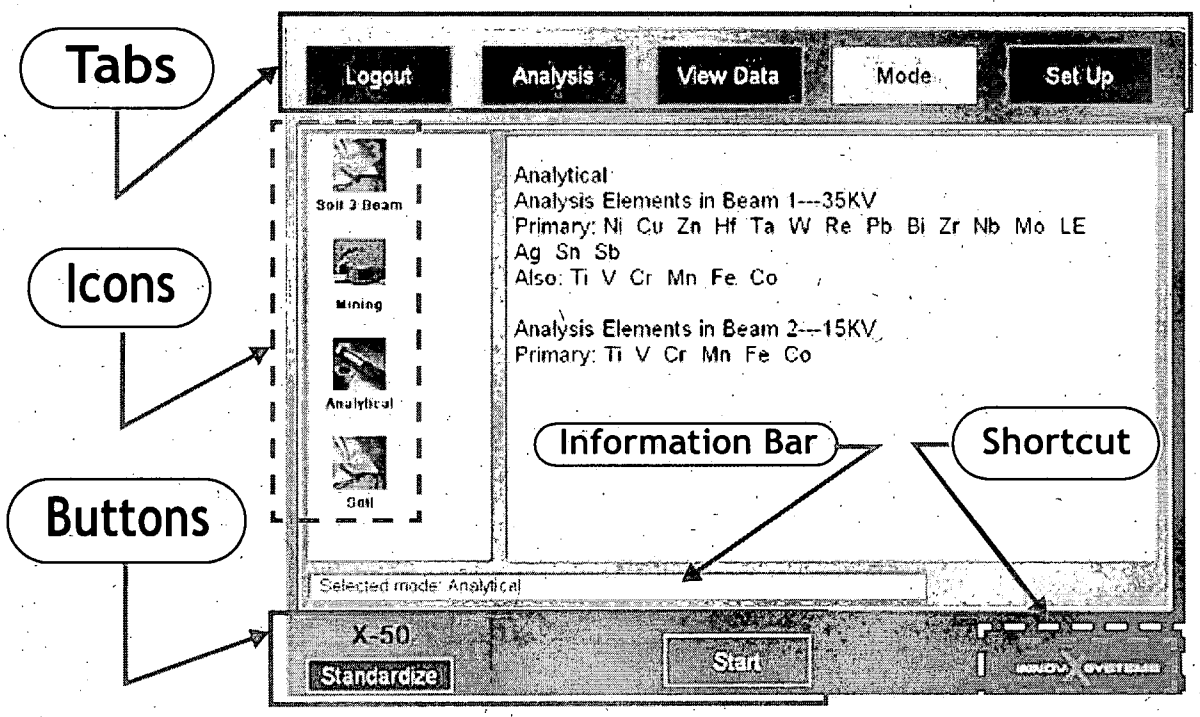



6. Press the *Login* button



## Navigating the Ver. 2.0 User Interface (2.0_UI)

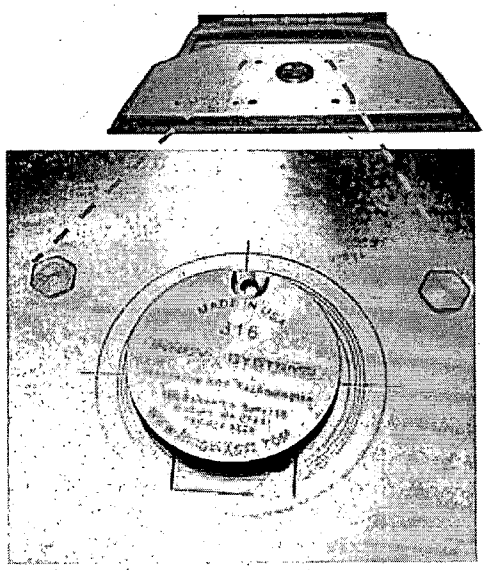



## Selecting Your Mode

By default the instrument starts up in the **last used** mode. If this is your desired current mode, continue with a Standardization or some other operation.
To change modes,

1. Press the Mode tab to invoke the screen shown above.
2. Choose your desired mode by selecting the appropriate Icon.

> **TIP** • An external keyboard and mouse may be applied via the USB ports.



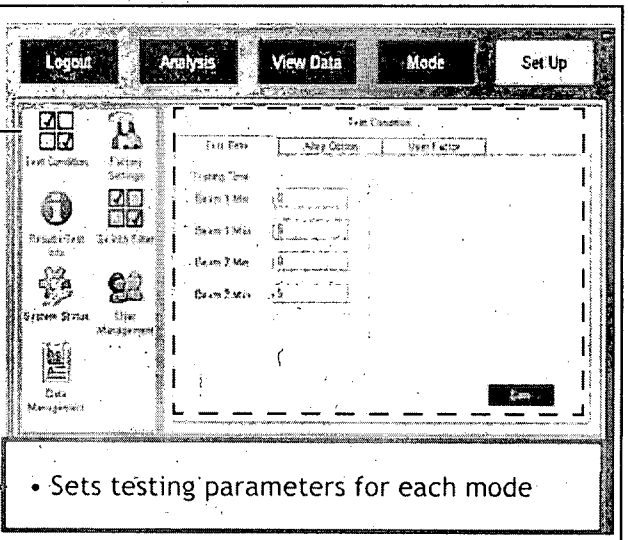
## Standardizing the Unit

1. Open the lid and place the Standardization Coupon over the measuring widow;
   – Ensure that it completely covers the window.
2. Close the lid.
3. Press *Standardize* on current 2.0_UI screen.
   The Information Bar reports the progress of the operation.
4. After completing successfully, open the lid and remove the Standardization Coupon.

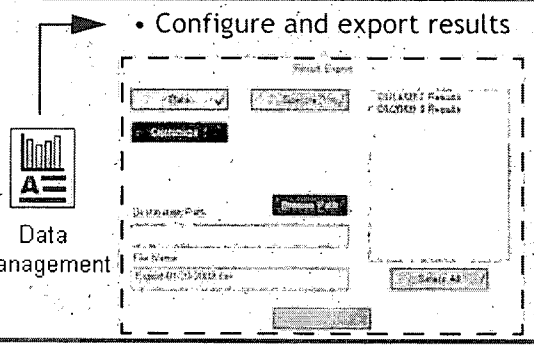
## Using the Set Up Facilities

The SETUP tab introduces several facilities.

Select an Icon to call the desired screen.

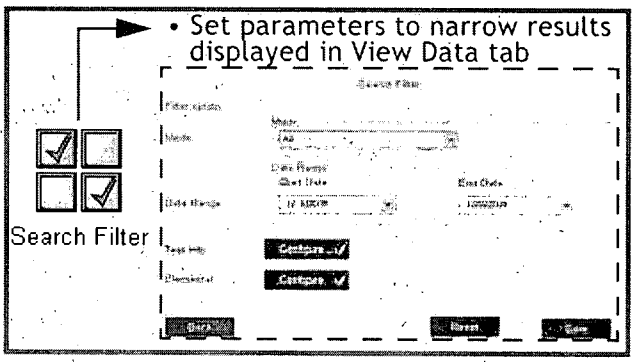



• Sets testing parameters for each mode



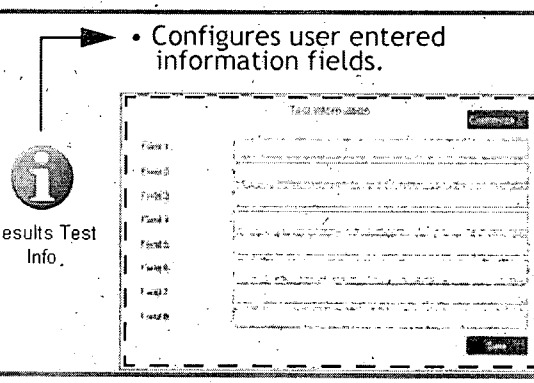
• Configure and export results

Data Management



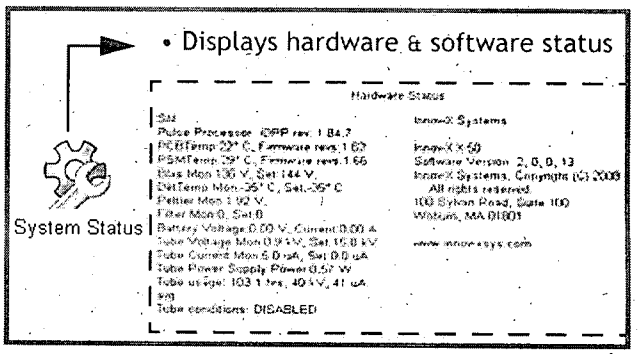
• Set parameters to narrow results displayed in View Data tab

Search Filter



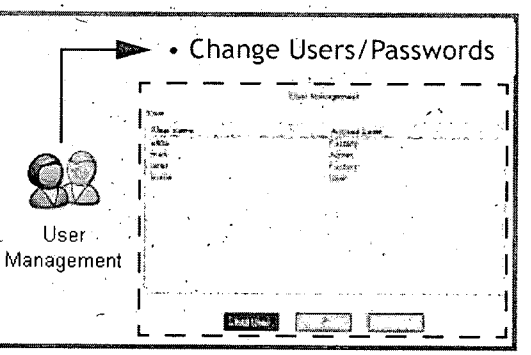
• Configures user entered information fields.

Results Test Info



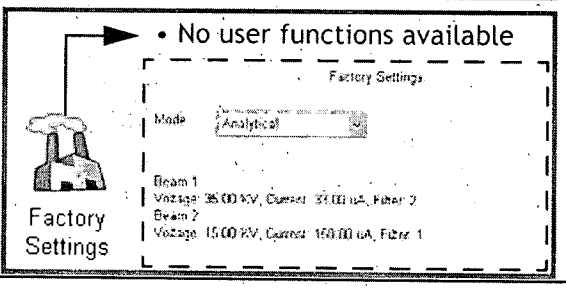
• Displays hardware & software status

System Status



• Change Users/Passwords

User Management

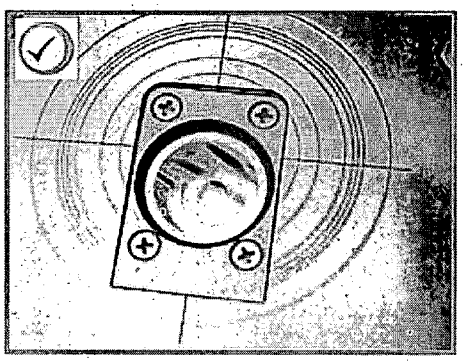


• No user functions available

Factory Settings

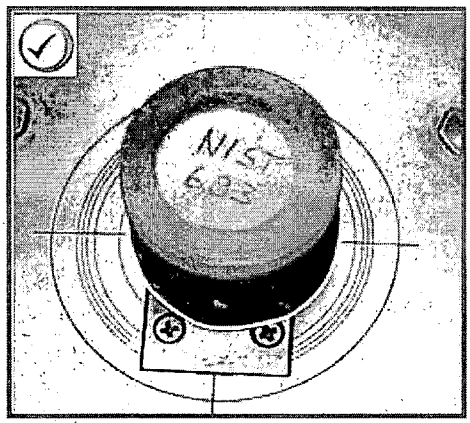
## Conducting a Test

1. Open lid.
2. Place sample over the measurement window.

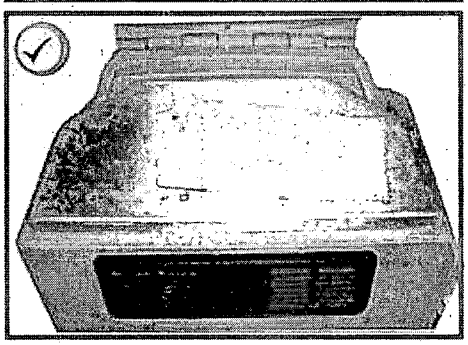


### TIPS

- **USE** the platform's engraved alignment rings and cross-hairs to position a test specimen for **accurate** and **repeatable** readings.
- When using sample cups, ensure that they are **FULL**.
- When employing a plastic bag to measure soil samples...
  - Arrange bag material so that at least a 2 cm thickness is over the window.
  - Try to use bags with very thin walls (low cost "store brands" are better than national brands)



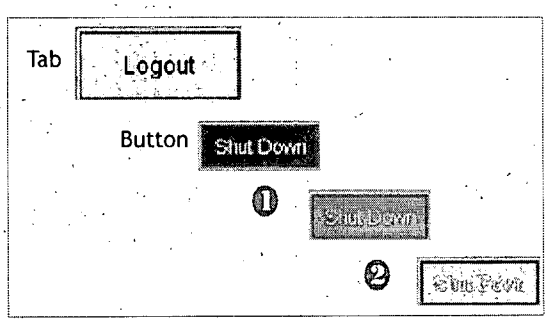

3. Close the lid.
4. Select *Start*
5. Testing begins, test status is displayed in Information Bar
   Results are available in several ways...
   a. Visually on Analysis screen.
   b. Saved to default internal hard disk.
   c. Exported to USB flash memory or network drive for later reporting and analysis.



## Shutdown Procedures

The recommended shutdown procedure is:

- Go to Logout Tab
  Double touch the *Shutdown* button
  - First press ① causes button to turn red, but no action occurs;
  - Second press ② button turns pink and executes the shutdown procedure



# Checking Results

## Analysis Tab

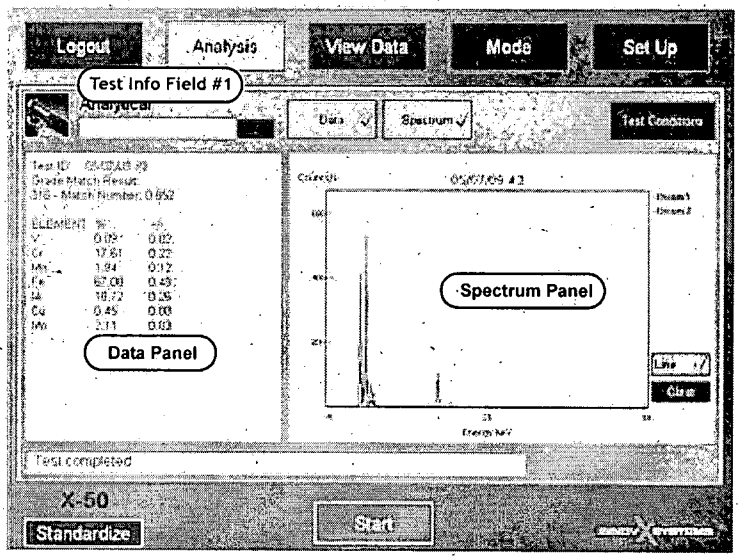
This tab displays the most recent result with the information reported in the data and spectrum panels.

Data panel shows a list of detected elements and their concentrations.

Touch a spectrum graph, the counts rate and energy at that point are displayed.

With the Line button toggled on, a touch on the spectral display shows the elemental energy lines in their appropriate locations.

The Clear button removes the lines.



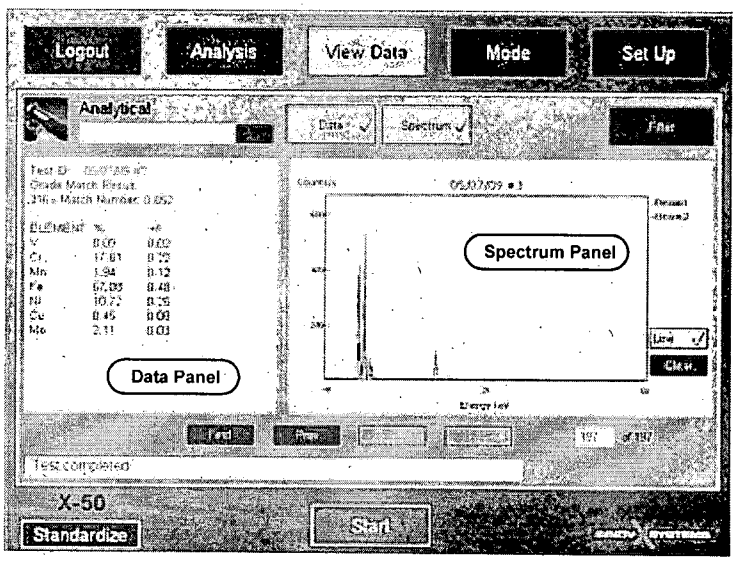

## View Data Tab

Select this tab to view ALL historical test results.

Similar to the Analysis tab, results are reported in the data and spectrum panels.

Navigation buttons allow an operator to examine the entire test results data set.

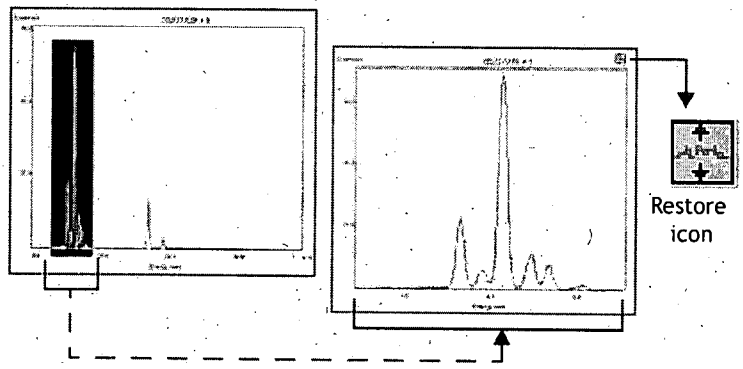
Filter button is a shortcut to the Search Filter screen of the Setup tab.




## TIPS

To expand certain plot areas, use your finger (or mouse) to select one corner and drag out the region of interest.

Press the Restore icon to bring the plot back to full scale.



# 6. Safety Administration

The *X-50* analyzer is a very safe instrument when used according to Innov-X's recommended safety procedures.

- Detectable radiation is below the limit for an uncontrolled area and is within regulatory limits.
- The x-ray tube has a multi-tiered safety interlock structure. See ***Product Safety Features, Page 4.***

Dosimeter

A dosimeter consists of a radiation-sensitive material packaged in a small container like a badge or ring.


Dosimeter
Badge Clip-on Style

Dosimeter
Ring Style

These devices record a person's accumulated radiation exposure over a period of time. It monitors workers using devices which emit ionizing radiation.

- Dosimeter badges are required by some states, and are optional with others.

Innov-X recommends that (at a minimum) all *X-50* analyzer operators wear badges/rings for the first year that their analyzer is in use.

# 7. Specifications

| Component | Description |
|---|---|
| Carry Case and Enclosure | • Rugged carry case with wheels and telescoping handle<br>• Analyzer enclosure is rugged injection molded multi-hinged unit<br>• Dimensions: Closed — 15/38 H x 12.5/32.8 W x 11/28 D [inches/centimeters]<br>• Dimensions: Open — 18/46 H x 12.5/32.8 W x 27/69 D [See *Page 3* for outline]<br>• Weight: 26 lbs/11 kg |
| Sample Chamber | • Dimensions: 11.3/28.7 W x 5.7/14.5 D x 4.5/11.4 H at front edge of platform.<br>• Lid has safety interlocks that create a closed beam system |
| Power Requirements | • 100 - 240 VAC, 50-60 Hz, auto switching power adapter; maximum draw less than 70 watts |
| Excitation System | • 50 kV, 200 uA X-ray tube |
| Primary Beam Filters | • Six position primary beam filters for optimal performance across the periodic table |
| Detection System | • High purity Si PiN detector delivers < 190 eV resolution |
| Computer | • Pentium processor with Windows® XP Embedded Runtime software; color touchscreen for display, mouse, and keyboard functions. I/O ports for external USB (2), serial, VGA devices, and network access. |
| Operating Environment | • Temperature: 0 - 50°C<br>• Humidity: 10 - 90% Relative Humidity, non-condensing |

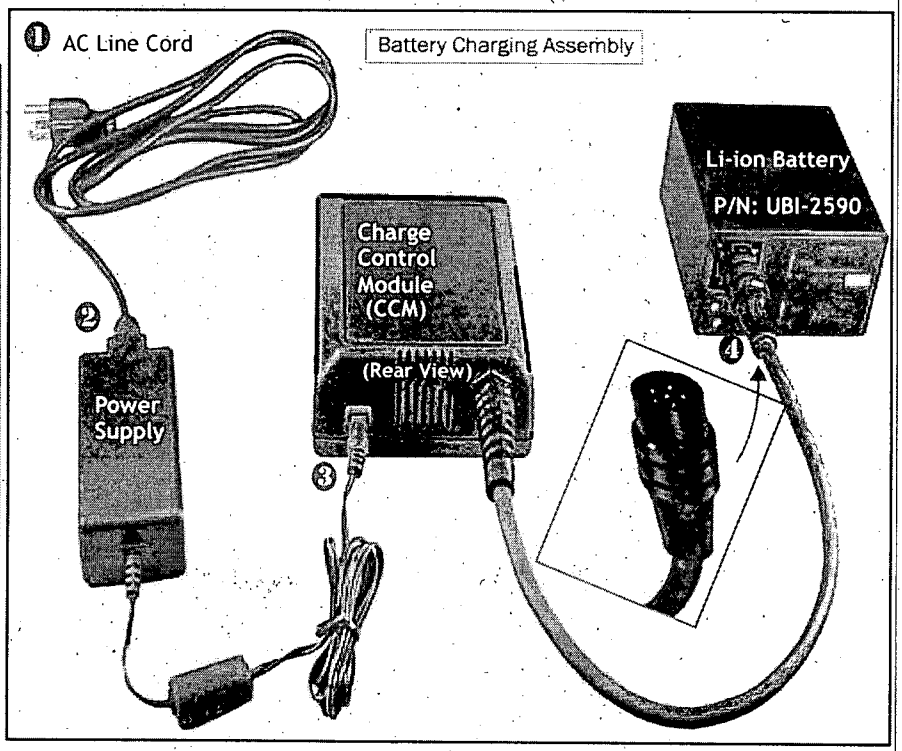
# 8. Battery Option

For complete mobile functionality, the X-50 can be outfitted with a rechargeable military-grade lithium-ion battery.
The battery is initially shipped with a charged condition between 50 and 70% of capacity.

Innov-X recommends that you completely charge the battery as soon as practical. Instructions are shown below. A Charge Control Module (CCM) manages the power to the battery. Charging to 100% takes approximately three hours. The CCM prevents over-charging.

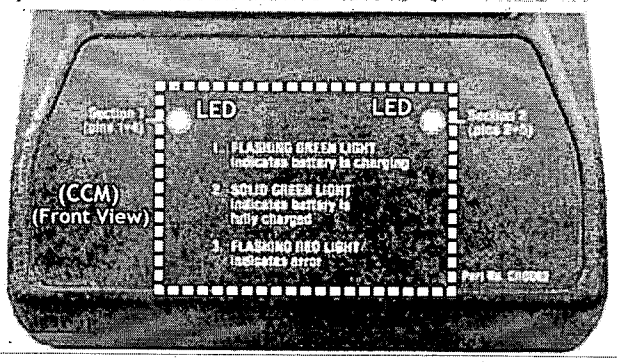
INSTRUCTIONS:
**Battery Charging**

1. Plug AC line cord into grounded power source.
2. Insert cord socket into the Power Supply
3. Insert DC Output into Charge Control Module DC Input Socket.
4. Insert CCM DC Output Connector into the Battery Input Socket. -Ensure that the pins and guides are aligned.

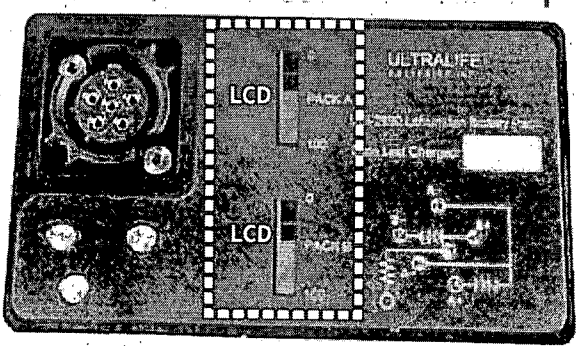



STATUS:
**Battery Charge**

Two LED indicators on the front of the CCM show the status of the charging cycle.

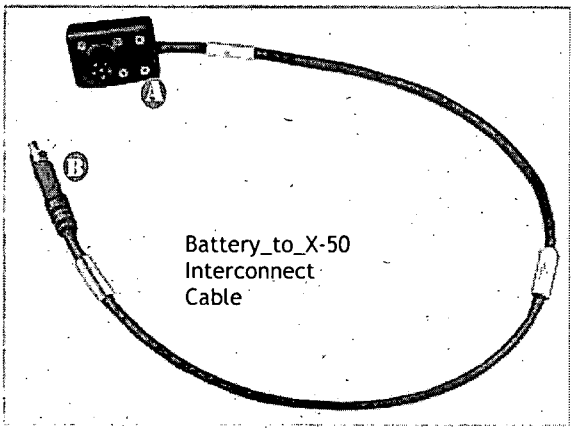


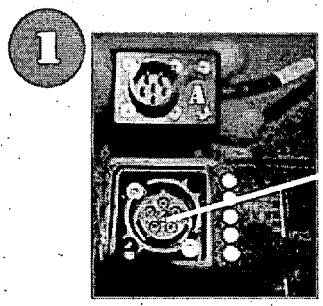

Two LCD indicators on the battery display the percent of capacity now available.

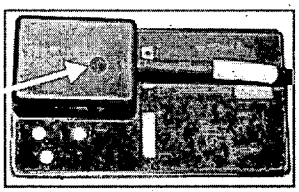


INSTRUCTIONS:
**Battery Connection**

1. Using the Interconnect Cable, plug connector (A) into battery socket.
2. Lift rubber cover over the X-50 Power socket.
3. Insert DC Output jack (B) into Power socket.

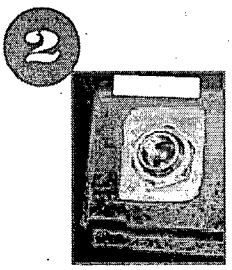


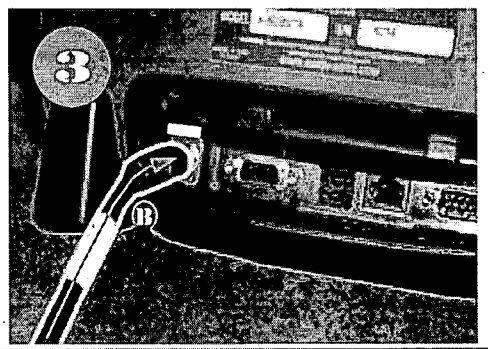



**⚠ WARNING**

- NEVER puncture, drop, crush, throw, hit, open, or modify the battery or casing.
- Do NOT incinerate.
- Do NOT submerge this product in water or any liquid.




**CAUTION**

When shipping this Li-ion battery, always observe all local transportation regulations.

# 10. Packing and Return Shipping

**If the instrument is not returned in the protective case, it can be damaged during shipping. Innov-X Systems reserves the right to void the warranty on instruments shipped without the protective case that are damaged during shipping. Prior to returning a unit, to receive the required RMA number and to answer any shipping questions, call Customer Service at 781-938-5005.**

Follow these instructions to return your XRF Analyzer:

1. Pack the analyzer in the black protective case in which it arrived, using the original packing materials.
2. Include the RMA in the case and reference the RMA number in your shipping documents.
3. Close the protective case and either:
   - Secure it with plastic zip ties, or
   - Pack the protective case within another box.

METHOD 6200

# FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

## 1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed below for soil and sediment samples. Some common elements are not listed in this method because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). These light elements are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed below are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF. The following RCRA analytes have been determined by this method:

| Analytes | CAS Registry No. |
|---|---|
| Antimony (Sb) | 7440-36-0 |
| Arsenic (As) | 7440-38-0 |
| Barium (Ba) | 7440-39-3 |
| Cadmium (Cd) | 7440-43-9 |
| Chromium (Cr) | 7440-47-3 |
| Cobalt (Co) | 7440-48-4 |
| Copper (Cu) | 7440-50-8 |
| Lead (Pb) | 7439-92-1 |
| Mercury (Hg) | 7439-97-6 |
| Nickel (Ni) | 7440-02-0 |
| Selenium (Se) | 7782-49-2 |
| Silver (Ag) | 7440-22-4 |
| Thallium (Tl) | 7440-28-0 |
| Tin (Sn) | 7440-31-5 |

| Analytes | CAS Registry No. |
|---|---|
| Vanadium (V) | 7440-62-2 |
| Zinc (Zn) | 7440-66-6 |

In addition, the following non-RCRA analytes have been determined by this method:

| Analytes | CAS Registry No. |
|---|---|
| Calcium (Ca) | 7440-70-2 |
| Iron (Fe) | 7439-89-6 |
| Manganese (Mn) | 7439-96-5 |
| Molybdenum (Mo) | 7439-93-7 |
| Potassium (K) | 7440-09-7 |
| Rubidium (Rb) | 7440-17-7 |
| Strontium (Sr) | 7440-24-6 |
| Thorium (Th) | 7440-29-1 |
| Titanium (Ti) | 7440-32-6 |
| Zirconium (Zr) | 7440-67-7 |

1.2 This method is a screening method to be used with confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)). This method's main strength is that it is a rapid field screening procedure. The method's lower limits of detection are typically above the toxicity characteristic regulatory level for most RCRA analytes. However, when the obtainable values for precision, accuracy, and laboratory-established sensitivity of this method meet project-specific data quality objectives (DQOs), FPXRF is a fast, powerful, cost effective technology for site characterization.

1.3 The method sensitivity or lower limit of detection depends on several factors, including the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. Example lower limits of detection for analytes of interest in environmental applications are shown in Table 1. These limits apply to a clean spiked matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (100 -600 second) count times. These sensitivity values are given for guidance only and may not always be achievable, since they will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of performance-based sensitivity is presented in Sec. 9.6.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments, specifically, in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

## 3.0 DEFINITIONS

3.1 FPXRF -- Field portable x-ray fluorescence.

3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS -- Site-specific calibration standards.

3.4 FP -- Fundamental parameter.

3.5 ROI -- Region of interest.

METHOD 6200

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In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use either sealed radioisotope sources or x-ray tubes to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples. The three electron shells include the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α), beta (β), or gamma (γ) etc., which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a $K_\alpha$ line is produced by a vacancy in the K shell filled by an L shell electron, whereas a $K_\beta$ line is produced by a vacancy in the K shell filled by an M shell electron. The $K_\alpha$ transition is on average 6 to 7 times more probable than the $K_\beta$ transition; therefore, the $K_\alpha$ line is approximately 7 times more intense than the $K_\beta$ line for a given element, making the $K_\alpha$ line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines ($L_\alpha$ and $L_\beta$) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments, specifically, in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

## 3.0 DEFINITIONS

3.1 FPXRF -- Field portable x-ray fluorescence.

3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS -- Site-specific calibration standards.

3.4 FP -- Fundamental parameter.

3.5 ROI -- Region of interest.

3.6 SRM -- Standard reference material; a standard containing certified amounts of metals in soil or sediment.

3.7 eV -- Electron volt; a unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One, Chapter Three, and the manufacturer's instructions for other definitions that may be relevant to this procedure.

## 4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup (i.e., against the cup window), the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the $K_\beta$ line of element Z-1 with the $K_\alpha$ line of element Z. This is called the $K_\alpha/K_\beta$ interference. Because the $K_\alpha$:$K_\beta$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V $K_\alpha$ and $K_\beta$ energies are 4.95 and 5.43 keV, respectively, and the Cr $K_\alpha$ energy is 5.41 keV. The Fe $K_\alpha$ and $K_\beta$ energies are 6.40 and 7.06 keV, respectively, and the Co $K_\alpha$ energy is 6.92 keV. The difference between the V $K_\beta$ and Cr $K_\alpha$ energies is 20 eV, and the difference between the Fe $K_\beta$ and the Co $K_\alpha$ energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) $K_\alpha$/lead (Pb) $L_\alpha$ and sulfur (S) $K_\alpha$/Pb $M_\alpha$. In the As/Pb case, Pb can be measured from the Pb $L_\beta$ line, and As can be measured from either the As $K_\alpha$ or the As $K_\beta$ line; in this way the interference can be corrected. If the As $K_\beta$ line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As $K_\alpha$ line. If the As $K_\alpha$ line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in reporting of a "nondetect" or a "less than" value (e.g., <300 ppm) for As, regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-

atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as Method 3050, or a total digestion procedure, such as Method 3052, is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project-specific data quality objectives (DQOs).

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method (see Table 8), the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r often exceeding 0.95, except for barium and chromium). The critical factor is that the digestion procedure and analytical reference method used should meet the DQOs of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Sec. 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10° F. The operator should follow the manufacturer's recommendations for gain check frequency.

## 5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The user is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

NOTE: No MSDS applies directly to the radiation-producing instrument because that is covered under the Nuclear Regulatory Commission (NRC) or applicable state regulations.

5.2 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operator's manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals.

Licenses for radioactive materials are of two types, specifically: (1) a general license which is usually initiated by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) a specific license which is issued to named persons for the operation of radioactive instruments as required by local, state, or federal agencies. A copy of the radioactive material license (for specific licenses only) and leak tests should be present with the instrument at all times and available to local and national authorities upon request.

X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply, however, if the tube is properly positioned within the instrument, this is only a negligible risk. Any instrument (x-ray tube or radioisotope based) is capable of delivering an electric shock from the basic circuitry when the system is inappropriately opened.

5.3 Radiation monitoring equipment should be used with the handling and operation of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs or badges should be worn in the area of maximum exposure. The maximum permissible whole-body dose from occupational exposure is 5 Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

## 6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for

use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

6.1 FPXRF spectrometer -- An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation sources -- FPXRF instruments use either a sealed radioisotope source or an x-ray tube to provide the excitation source. Many FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron Fe-55 ($^{55}$Fe), cadmium Cd-109 ($^{109}$Cd), americium Am-241 ($^{241}$Am), and curium Cm-244 ($^{244}$Cm). These sources may be contained in a probe along with a window and the detector; the probe may be connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF analysis. The decay of radioisotopes is measured in "half-lives." The half-life of a radioisotope is defined as the length of time required to reduce the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. This is due to the ever increasing time required for the analysis rather than a decrease in instrument performance. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum necessary for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of

accelerating voltage is governed both by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material and by the instrument's ability to cool the x-ray tube. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample presentation device -- FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For FPXRF instruments operated in the intrusive mode, the probe may be rotated so that the window faces either upward or downward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors -- The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide ($HgI_2$), silicon pin diode and lithium-drifted silicon Si(Li). The $HgI_2$ detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The Si(Li) detector must be cooled to at least -90 °C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a Si(Li) detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 L. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese $K_\alpha$ peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: $HgI_2$-270 eV; silicon pin diode-250 eV; Si(Li)–170 eV; and gas-filled, proportional counter-750 eV.

During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data processing units -- The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in ppm on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 3,000 to 5,000 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software built into the

units or from PCs. Once the data–storage memory of an FPXRF unit is full or at any other time, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery and battery charger.

6.3 Polyethylene sample cups -- 31 to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film -- Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 µm thick.

6.5 Mortar and pestle -- Glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers -- Glass or plastic to store samples.

6.7 Sieves -- 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels -- For smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags -- Used for collection and homogenization of soil samples.

6.10 Drying oven -- Standard convection or toaster oven, for soil and sediment samples that require drying.

## 7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Pure element standards -- Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if designated for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.3 Site-specific calibration standards -- Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.3.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of 10 samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.3.2 Each sample should be oven-dried for 2 to 4 hr at a temperature of less than 150 °C. If mercury is to be analyzed, a separate sample portion should be dried at ambient temperature as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be homogenized (see Sec. 7.3.3) and then a representative portion ground with a mortar and pestle or other mechanical means, prior to passing through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.3.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 g of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 g of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.4 Blank samples -- The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the established lower limit of detection. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.5 Standard reference materials -- Standard reference materials (SRMs) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories. When these SRMs are unavailable, alternate standards may be used (e.g., NIST 2702).

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, "Inorganic Analytes."

## 9.0 QUALITY CONTROL

9.1 Follow the manufacturer's instructions for the quality control procedures specific to use of the testing product. Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

9.2 Energy calibration check -- To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting,

which would indicate drift within the instrument. As discussed in Sec. 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (more than 10 °F).

9.2.1 The energy calibration check should be run at a frequency consistent with manufacturer's recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.2 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak. The intensity and channel number of the pure element as measured using the source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank samples -- Two types of blank samples should be analyzed for FPXRF analysis, specifically, instrument blanks and method blanks.

9.3.1 An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window. The instrument blank can be silicon dioxide, a polytetraflurorethylene (PTFE) block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the established lower limit of detection should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of detection or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration verification checks -- A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ±20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision measurements -- The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent. If both in situ and intrusive analytical techniques are used during the course of one day, it is recommended that separate precision calculations be performed for each analysis type.

The equation for calculating RSD is as follows:

$$RSD = (SD/Mean\ Concentration) \times 100$$

where:

| | | |
|---|---|---|
| RSD | = | Relative standard deviation for the precision measurement for the analyte |
| SD | = | Standard deviation of the concentration for the analyte |
| Mean concentration | = | Mean concentration for the analyte |

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the sensitivity, but decreases sample throughput.

9.6 The lower limits of detection should be established from actual measured performance based on spike recoveries in the matrix of concern or from acceptable method performance on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity as opposed to a statistical determination based on the standard deviation of

replicate analyses of a low-concentration sample. While the statistical approach demonstrates the potential data variability for a given sample matrix at one point in time, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated. For this reason the sensitivity should be established as the lowest point of detection based on acceptable target analyte recovery in the desired sample matrix.

9.7 Confirmatory samples -- The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory samples must be splits of the well homogenized sample material. In some cases the prepared sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on project-specific data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument calibration -- Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments, namely: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental parameters calibration -- FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are necessary, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are necessary.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Sec. 7.3. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective energy FP calibration -- The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ±20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ±20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference
$C_k$ = Certified concentration of standard sample
$C_s$ = Measured concentration of standard sample

10.2.2 BFP calibration -- BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended

count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ±20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ±20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical calibration -- An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Sec. 7.3; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is necessary. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are necessary to perform an adequate empirical calibration. The exact number of standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton normalization method -- The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline reading. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton $K_{\alpha}$ peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

## 11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later during analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, remove any large or nonrepresentative debris from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Also, the soil surface must be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide example performance data for this method, this modest amount of sample preparation was found to take less than 5 min per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for in situ analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on the desired method sensitivity. Due to the heterogeneous nature of the soil sample, in situ analysis can provide only "screening" type data.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 g or 250 $cm^3$, which is enough soil to fill an 8-ounce jar. However, the exact dimensions and sample depth should take into consideration the heterogeneous deposition of contaminants and will ultimately depend on the desired project-specific data quality objectives. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Sec. 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the time necessary for homogenization procedure using the fluorescein dye ranged from 3 to 5 min per sample. As demonstrated in Secs. 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, the direct analysis through the plastic bag is possible without the more labor intensive steps of drying, grinding, and sieving given in Secs. 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps should be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 °C. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 min per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 µm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle, and sieves must be thoroughly cleaned so that any cross-contamination is below the established lower limit of detection of the procedure or DQOs of the analysis. If all recommended sample preparation steps are followed, there is a high probability the desired laboratory data quality may be obtained.

## 12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in ppm and can be downloaded to a personal computer, which can be used to provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation. See the manufacturer's instructions regarding data analysis and calculations.

## 13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The sections to follow discuss three performance evaluation factors; namely, precision, accuracy, and comparability. The example data presented in Tables 4 through 8 were generated from results obtained from six FPXRF instruments (see Sec. 13.3). The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from "nondetect" to tens of thousands of mg/kg. These data are provided for guidance purposes only.

13.3 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a $HgI_2$ detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode

detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.4 All example data presented in Tables 4 through 8 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.5 Precision measurements -- The example precision data are presented in Table 4. These data are provided for guidance purposes only. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from "nondetects" to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 4 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the lower limit of detection for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 4. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the lower limit of detection so that an RSD value calculated at 5 to 10 times this limit was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 5 shows these results. These data are provided for guidance purposes only. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the lower limit of detection for the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the in situ homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 5 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square,

measurements of different soil samples were actually taking place within the square. Table 5 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five instead of ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy measurements -- Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 6 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 6 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 6. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 6.

Table 7 provides a more detailed summary of accuracy data for one particular FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. These data are provided for guidance purposes only. Table 7 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability -- Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination ($r^2$).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 8. Similar trends in the data were seen for all instruments. These data are provided for guidance purposes only.

Table 8 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. These data are provided for guidance purposes only. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--intrusive, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not

ground; and preparation 4–intrusive, with sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with $r^2$ values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The $r^2$ values and slopes of the regression lines for barium and chromium were not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 8 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 8 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Sec. 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time necessary to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 min. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 min per sample. Lastly, when grinding and sieving is conducted, time has to be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 A. D. Hewitt, "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton $K_\alpha$ Peak Normalization Analysis," American Environmental Laboratory, pp 24-32, 1994.

13.8.2 S. Piorek and J. R. Pasmore, "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer," Third International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals, Las Vegas, Nevada, February 24-26, 1993, Vol 2, pp 1135-1151, 1993.

13.8.3 S. Shefsky, "Sample Handling Strategies for Accurate Lead-in-soil Measurements in the Field and Laboratory," *International Symposium of Field Screening Methods for Hazardous Waste and Toxic Chemicals*, Las Vegas, NV, January 29-31, 1997.

## 14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

## 15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

## 16.0 REFERENCES


1. Metorex, X-MET 920 User's Manual.

2. Spectrace Instruments, "Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction," 1994.

3. TN Spectrace, Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.

4. Unpublished SITE data, received from PRC Environment Management, Inc.


## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE INTERFERENCE FREE LOWER LIMITS OF DETECTION

| Analyte | Chemical Abstract Series Number | Lower Limit of Detection in Quartz Sand (milligrams per kilogram) |
|---|---|---|
| Antimony (Sb) | 7440-36-0 | 40 |
| Arsenic (As) | 7440-38-0 | 40 |
| Barium (Ba) | 7440-39-3 | 20 |
| Cadmium (Cd) | 7440-43-9 | 100 |
| Calcium (Ca) | 7440-70-2 | 70 |
| Chromium (Cr) | 7440-47-3 | 150 |
| Cobalt (Co) | 7440-48-4 | 60 |
| Copper (Cu) | 7440-50-8 | 50 |
| Iron (Fe) | 7439-89-6 | 60 |
| Lead (Pb) | 7439-92-1 | 20 |
| Manganese (Mn) | 7439-96-5 | 70 |
| Mercury (Hg) | 7439-97-6 | 30 |
| Molybdenum (Mo) | 7439-93-7 | 10 |
| Nickel (Ni) | 7440-02-0 | 50 |
| Potassium (K) | 7440-09-7 | 200 |
| Rubidium (Rb) | 7440-17-7 | 10 |
| Selenium (Se) | 7782-49-2 | 40 |
| Silver (Ag) | 7440-22-4 | 70 |
| Strontium (Sr) | 7440-24-6 | 10 |
| Thallium (Tl) | 7440-28-0 | 20 |
| Thorium (Th) | 7440-29-1 | 10 |
| Tin (Sn) | 7440-31-5 | 60 |
| Titanium (Ti) | 7440-32-6 | 50 |
| Vanadium (V) | 7440-62-2 | 50 |
| Zinc (Zn) | 7440-66-6 | 50 |
| Zirconium (Zr) | 7440-67-7 | 10 |

Source: Refs. 1, 2, and 3
These data are provided for guidance purposes only.

TABLE 2

SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS

| Source | Activity (mCi) | Half-Life (Years) | Excitation Energy (keV) | Elemental Analysis Range | |
|---|---|---|---|---|---|
| Fe-55 | 20-50 | 2.7 | 5.9 | Sulfur to Chromium<br>Molybdenum to Barium | K Lines<br>L Lines |
| Cd-109 | 5-30 | 1.3 | 22.1 and 87.9 | Calcium to Rhodium<br>Tantalum to Lead<br>Barium to Uranium | K Lines<br>K Lines<br>L Lines |
| Am-241 | 5-30 | 432 | 26.4 and 59.6 | Copper to Thulium<br>Tungsten to Uranium | K Lines<br>L Lines |
| Cm-244 | 60-100 | 17.8 | 14.2 | Titanium to Selenium<br>Lanthanum to Lead | K Lines<br>L Lines |

Source:. Refs. 1, 2, and 3

TABLE 3

SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS

| Anode Material | Recommended Voltage Range (kV) | K-alpha Emission (keV) | Elemental Analysis Range | |
|---|---|---|---|---|
| Cu | 18-22 | 8.04 | Potassium to Cobalt<br>Silver to Gadolinium | K Lines<br>L Lines |
| Mo | 40-50 | 17.4 | Cobalt to Yttrium<br>Europium to Radon | K Lines<br>L Lines |
| Ag | 50-65 | 22.1 | Zinc to Technicium<br>Ytterbium to Neptunium | K Lines<br>L Lines |

Source: Ref. 4

Notes: The sample elements excited are chosen by taking as the lower limit the same ratio of excitation line energy to element absorption edge as in Table 2 (approximately 0.45) and the requirement that the excitation line energy be above the element absorption edge as the upper limit (L2 edges used for L lines). K-beta excitation lines were ignored.

TABLE 4

EXAMPLE PRECISION VALUES

| Analyte | Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the Lower Limit of Detection | | | | | |
|---|---|---|---|---|---|---|
| | TN 9000 | TN Lead Analyzer | X-MET 920 (SiLi Detector) | X-MET 920 (Gas-Filled Detector) | XL Spectrum Analyzer | MAP Spectrum Analyzer |
| Antimony | 6.54 | NR | NR | NR | NR | NR |
| Arsenic | 5.33 | 4.11 | 3.23 | 1.91 | 12.47 | 6.68 |
| Barium | 4.02 | NR | 3.31 | 5.91 | NR | NR |
| Cadmium | 29.84[a] | NR | 24.80[a] | NR | NR | NR |
| Calcium | 2.16 | NR | NR | NR | NR | NR |
| Chromium | 22.25 | 25.78 | 22.72 | 3.91 | 30.25 | NR |
| Cobalt | 33.90 | NR | NR | NR | NR | NR |
| Copper | 7.03 | 9.11 | 8.49 | 9.12 | 12.77 | 14.86 |
| Iron | 1.78 | 1.67 | 1.55 | NR | 2.30 | NR |
| Lead | 6.45 | 5.93 | 5.05 | 7.56 | 6.97 | 12.16 |
| Manganese | 27.04 | 24.75 | NR | NR | NR | NR |
| Molybdenum | 6.95 | NR | NR | NR | 12.60 | NR |
| Nickel | 30.85[a] | NR | 24.92[a] | 20.92[a] | NA | NR |
| Potassium | 3.90 | NR | NR | NR | NR | NR |
| Rubidium | 13.06 | NR | NR | NR | 32.69[a] | NR |
| Strontium | 4.28 | NR | NR | NR | 8.86 | NR |
| Tin | 24.32[a] | NR | NR | NR | NR | NR |
| Titanium | 4.87 | NR | NR | NR | NR | NR |
| Zinc | 7.27 | 7.48 | 4.26 | 2.28 | 10.95 | 0.83 |
| Zirconium | 3.58 | NR | NR | NR | 6.49 | NR |

These data are provided for guidance purposes only.
Source: Ref. 4

[a] These values are biased high because the concentration of these analytes in the soil samples was near the lower limit of detection for that particular FPXRF instrument.

NR Not reported.

NA Not applicable; analyte was reported but was below the established lower limit detection.

TABLE 5

EXAMPLES OF PRECISION AS AFFECTED BY SAMPLE PREPARATION

| Analyte | Average Relative Standard Deviation for Each Preparation Method | | |
|---|---|---|---|
| | In Situ-Field | Intrusive-Undried and Unground | Intrusive-Dried and Ground |
| Antimony | 30.1 | 15.0 | 14.4 |
| Arsenic | 22.5 | 5.36 | 3.76 |
| Barium | 17.3 | 3.38 | 2.90 |
| Cadmium[a] | 41.2 | 30.8 | 28.3 |
| Calcium | 17.5 | 1.68 | 1.24 |
| Chromium | 17.6 | 28.5 | 21.9 |
| Cobalt | 28.4 | 31.1 | 28.4 |
| Copper | 26.4 | 10.2 | 7.90 |
| Iron | 10.3 | 1.67 | 1.57 |
| Lead | 25.1 | 8.55 | 6.03 |
| Manganese | 40.5 | 12.3 | 13.0 |
| Mercury | ND | ND | ND |
| Molybdenum | 21.6 | 20.1 | 19.2 |
| Nickel[a] | 29.8 | 20.4 | 18.2 |
| Potassium | 18.6 | 3.04 | 2.57 |
| Rubidium | 29.8 | 16.2 | 18.9 |
| Selenium | ND | 20.2 | 19.5 |
| Silver[a] | 31.9 | 31.0 | 29.2 |
| Strontium | 15.2 | 3.38 | 3.98 |
| Thallium | 39.0 | 16.0 | 19.5 |
| Thorium | NR | NR | NR |
| Tin | ND | 14.1 | 15.3 |
| Titanium | 13.3 | 4.15 | 3.74 |
| Vanadium | NR | NR | NR |
| Zinc | 26.6 | 13.3 | 11.1 |
| Zirconium | 20.2 | 5.63 | 5.18 |

These data are provided for guidance purposes only.
Source: Ref. 4
[a] These values may be biased high because the concentration of these analytes in the soil samples was near the lower limit of detection.
ND Not detected.
NR Not reported.

TABLE 6

EXAMPLE ACCURACY VALUES

| Analyte | Instrument | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TN 9000 | | | | TN Lead Analyzer | | | | X-MET 920 (SiLi Detector) | | | | XL Spectrum Analyzer | | | |
| | n | Range of % Rec. | Mean % Rec. | SD | n | Range of % Rec. | Mean % Rec. | SD | n | Range of % Rec. | Mean % Rec | SD | n | Range of % Rec. | Mean % Rec. | SD |
| Sb | 2 | 100-149 | 124.3 | NA | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| As | 5 | 68-115 | 92.8 | 17.3 | 5 | 44-105 | 83.4 | 23.2 | 4 | 9.7-91 | 47.7 | 39.7 | 5 | 38-535 | 189.8 | 206 |
| Ba | 9 | 98-198 | 135.3 | 36.9 | -- | -- | -- | -- | 9 | 18-848 | 168.2 | 262 | -- | -- | -- | -- |
| Cd | 2 | 99-129 | 114.3 | NA | -- | -- | -- | -- | 6 | 81-202 | 110.5 | 45.7 | -- | -- | -- | -- |
| Cr | 2 | 99-178 | 138.4 | NA | -- | -- | -- | -- | 7 | 22-273 | 143.1 | 93.8 | 3 | 98-625 | 279.2 | 300 |
| Cu | 8 | 61-140 | 95.0 | 28.8 | 6 | 38-107 | 79.1 | 27.0 | 11 | 10-210 | 111.8 | 72.1 | 8 | 95-480 | 203.0 | 147 |
| Fe | 6 | 78-155 | 103.7 | 26.1 | 6 | 89-159 | 102.3 | 28.6 | 6 | 48-94 | 80.4 | 16.2 | 6 | 26-187 | 108.6 | 52.9 |
| Pb | 11 | 66-138 | 98.9 | 19.2 | 11 | 68-131 | 97.4 | 18.4 | 12 | 23-94 | 72.7 | 20.9 | 13 | 80-234 | 107.3 | 39.9 |
| Mn | 4 | 81-104 | 93.1 | 9.70 | 3 | 92-152 | 113.1 | 33.8 | -- | -- | -- | -- | -- | -- | -- | -- |
| Ni | 3 | 99-122 | 109.8 | 12.0 | -- | -- | -- | -- | -- | -- | -- | -- | 3 | 57-123 | 87.5 | 33.5 |
| Sr | 8 | 110-178 | 132.6 | 23.8 | -- | -- | -- | -- | -- | -- | -- | -- | 7 | 86-209 | 125.1 | 39.5 |
| Zn | 11 | 41-130 | 94.3 | 24.0 | 10 | 81-133 | 100.0 | 19.7 | 12 | 46-181 | 106.6 | 34.7 | 11 | 31-199 | 94.6 | 42.5 |

Source: Ref. 4. These data are provided for guidance purposes only.
n: Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.
SD: Standard deviation; NA: Not applicable; only two data points, therefore, a SD was not calculated.
%Rec.: Percent recovery.
-- No data.

TABLE 7

EXAMPLE ACCURACY FOR TN 9000[a]

| Standard Reference Material | Arsenic | | | Barium | | | Copper | | | Lead | | | Zinc | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. |
| RTC CRM-021 | 24.8 | ND | NA | 586 | 1135 | 193.5 | 4792 | 2908 | 60.7 | 144742 | 149947 | 103.6 | 546 | 224 | 40.9 |
| RTC CRM-020 | 397 | 429 | 92.5 | 22.3 | ND | NA | 753 | 583 | 77.4 | 5195 | 3444 | 66.3 | 3022 | 3916 | 129.6 |
| BCR CRM 143R | -- | -- | -- | -- | -- | -- | 131 | 105 | 80.5 | 180 | 206 | 114.8 | 1055 | 1043 | 99.0 |
| BCR CRM 141 | -- | -- | -- | -- | -- | -- | 32.6 | ND | NA | 29.4 | ND | NA | 81.3 | ND | NA |
| USGS GXR-2 | 25.0 | ND | NA | 2240 | 2946 | 131.5 | 76.0 | 106 | 140.2 | 690 | 742 | 107.6 | 530 | 596 | 112.4 |
| USGS GXR-6 | 330 | 294 | 88.9 | 1300 | 2581 | 198.5 | 66.0 | ND | NA | 101 | 80.9 | 80.1 | 118 | ND | NA |
| NIST 2711 | 105 | 104 | 99.3 | 726 | 801 | 110.3 | 114 | ND | NA | 1162 | 1172 | 100.9 | 350 | 333 | 94.9 |
| NIST 2710 | 626 | 722 | 115.4 | 707 | 782 | 110.6 | 2950 | 2834 | 96.1 | 5532 | 5420 | 98.0 | 6952 | 6476 | 93.2 |
| NIST 2709 | 17.7 | ND | NA | 968 | 950 | 98.1 | 34.6 | ND | NA | 18.9 | ND | NA | 106 | 98.5 | 93.0 |
| NIST 2704 | 23.4 | ND | NA | 414 | 443 | 107.0 | 98.6 | 105 | 106.2 | 161 | 167 | 103.5 | 438 | 427 | 97.4 |
| CNRC PACS-1 | 211 | 143 | 67.7 | -- | 772 | NA | 452 | 302 | 66.9 | 404 | 332 | 82.3 | 824 | 611 | 74.2 |
| SARM-51 | -- | -- | -- | 335 | 466 | 139.1 | 268 | 373 | 139.2 | 5200 | 7199 | 138.4 | 2200 | 2676 | 121.6 |
| SARM-52 | -- | -- | -- | 410 | 527 | 128.5 | 219 | 193 | 88.1 | 1200 | 1107 | 92.2 | 264 | 215 | 81.4 |

Source: Ref. 4. These data are provided for guidance purposes only.

[a] All concentrations in milligrams per kilogram.

%Rec.: Percent recovery; ND: Not detected; NA: Not applicable.

-- No data.

TABLE 8

EXAMPLE REGRESSION PARAMETERS FOR COMPARABILITY[1]

| | Arsenic | | | | Barium | | | | Copper | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope |
| All Data | 824 | 0.94 | 1.62 | 0.94 | 1255 | 0.71 | 60.3 | 0.54 | 984 | 0.93 | 2.19 | 0.93 |
| Soil 1 | 368 | 0.96 | 1.41 | 0.95 | 393 | 0.05 | 42.6 | 0.11 | 385 | 0.94 | 1.26 | 0.99 |
| Soil 2 | 453 | 0.94 | 1.51 | 0.96 | 462 | 0.56 | 30.2 | 0.66 | 463 | 0.92 | 2.09 | 0.95 |
| Soil 3 | — | — | — | — | 400 | 0.85 | 44.7 | 0.59 | 136 | 0.46 | 16.60 | 0.57 |
| Prep 1 | 207 | 0.87 | 2.69 | 0.85 | 312 | 0.64 | 53.7 | 0.55 | 256 | 0.87 | 3.89 | 0.87 |
| Prep 2 | 208 | 0.97 | 1.38 | 0.95 | 315 | 0.67 | 64.6 | 0.52 | 246 | 0.96 | 2.04 | 0.93 |
| Prep 3 | 204 | 0.96 | 1.20 | 0.99 | 315 | 0.78 | 64.6 | 0.53 | 236 | 0.97 | 1.45 | 0.99 |
| Prep 4 | 205 | 0.96 | 1.45 | 0.98 | 313 | 0.81 | 58.9 | 0.55 | 246 | 0.96 | 1.99 | 0.96 |

| | Lead | | | | Zinc | | | | Chromium | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope |
| All Data | 1205 | 0.92 | 1.66 | 0.95 | 1103 | 0.89 | 1.86 | 0.95 | 280 | 0.70 | 64.6 | 0.42 |
| Soil 1 | 357 | 0.94 | 1.41 | 0.96 | 329 | 0.93 | 1.78 | 0.93 | — | — | — | — |
| Soil 2 | 451 | 0.93 | 1.62 | 0.97 | 423 | 0.85 | 2.57 | 0.90 | — | — | — | — |
| Soil 3 | 397 | 0.90 | 2.40 | 0.90 | 351 | 0.90 | 1.70 | 0.98 | 186 | 0.66 | 38.9 | 0.50 |
| Prep 1 | 305 | 0.80 | 2.88 | 0.86 | 286 | 0.79 | 3.16 | 0.87 | 105 | 0.80 | 66.1 | 0.43 |
| Prep 2 | 298 | 0.97 | 1.41 | 0.96 | 272 | 0.95 | 1.86 | 0.93 | 77 | 0.51 | 81.3 | 0.36 |
| Prep 3 | 302 | 0.98 | 1.26 | 0.99 | 274 | 0.93 | 1.32 | 1.00 | 49 | 0.73 | 53.7 | 0.45 |
| Prep 4 | 300 | 0.96 | 1.38 | 1.00 | 271 | 0.94 | 1.41 | 1.01 | 49 | 0.75 | 31.6 | 0.56 |

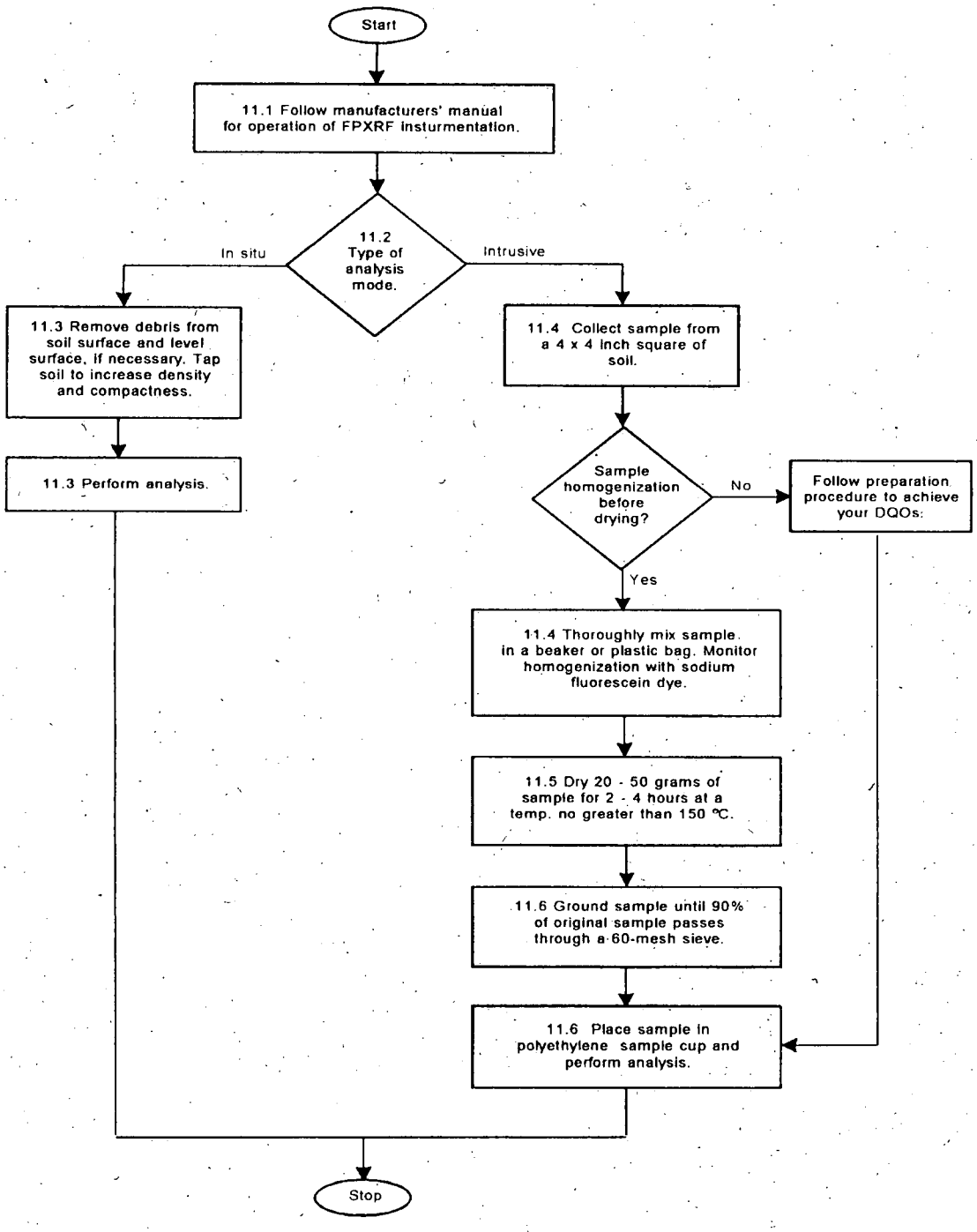
Source: Ref. 4. These data are provided for guidance purposes only.

[1] Log-transformed data

n: Number of data points; $r^2$: Coefficient of determination; Int.: Y-intercept

— No applicable data

# FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT



# LEAD by Flame AAS 7082

Pb MW: 207.19 (Pb) 223.19 (PbO) CAS: 7439-92-1 (Pb) 1317-36-8 (PbO) RTECS: OF7525000 (Pb) OG1750000 (PbO)

**METHOD: 7082, Issue 2** **EVALUATION: FULL** **Issue 1: 15 February 1984 Issue 2: 15 August 1994**

**OSHA :** 0.05 mg/m$^3$
**NIOSH:** <0.1 mg/m$^3$; blood Pb ≤60 µg/100 g
**ACGIH:** 0.05 mg/m$^3$

**PROPERTIES:** soft metal; d 11.3 g/cm$^3$; MP 327.5 °C; valences +2, +4 in salts

**SYNONYMS:** elemental lead and lead compounds except alkyl lead

## SAMPLING

| | |
|---|---|
| **SAMPLER:** | FILTER (0.8-µm cellulose ester membrane) |
| **FLOW RATE:** | 1 to 4 L/min |
| **VOL-MIN:** | 200 L @ 0.05 mg/m$^3$ |
| **-MAX:** | 1500 L |
| **SHIPMENT:** | routine |
| **SAMPLE STABILITY:** | stable |
| **BLANKS:** | 2 to 10 field blanks per set |

## ACCURACY

| | |
|---|---|
| **RANGE STUDIED:** | 0.13 to 0.4 mg/m$^3$ [1]; 0.15 to 1.7 mg/m$^3$ (fume) [2] |
| **BIAS:** | - 3.1% |
| **OVERALL PRECISION($\hat{S}_{rT}$):** | 0.072 [1]; 0.068 (fume) [2] |
| **ACCURACY:** | ± 17.6% |

## MEASUREMENT

| | |
|---|---|
| **TECHNIQUE:** | ATOMIC ABSORPTION SPECTROPHOTOMETER, FLAME |
| **ANALYTE:** | lead |
| **ASHING:** | conc. $HNO_3$, 6 mL + 30% $H_2O_2$, 1 mL; 140 °C |
| **FINAL SOLUTION:** | 10% $HNO_3$, 10 mL |
| **FLAME:** | air-acetylene, oxidizing |
| **WAVELENGTH:** | 283.3 nm |
| **BACKGROUND CORRECTION:** | $D_2$ or $H_2$ lamp, or Zeeman |
| **CALIBRATION:** | $Pb^{2+}$ in 10% $HNO_3$ |
| **RANGE** | 10 to 200 µg per sample [2,3] |
| **ESTIMATED LOD:** | 2.6 µg per sample [4] |
| **PRECISION ($\hat{S}_r$):** | 0.03 [1] |

**APPLICABILITY:** The working range is 0.05 to >1 mg/m$^3$ for a 200-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

**INTERFERENCES:** Use $D_2$ or $H_2$ continuum or Zeeman background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

**OTHER METHODS:** This method combines and replaces P&CAM 173 [3] and S341 [4,5] for lead. Method 7300 (ICP-AES) and 7105 (AAS/GF) are alternate analytical methods. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [5] and the lead criteria document [6]; and P&CAM 191 (ASV) [7].

**REAGENTS:**

1. Nitric acid, conc.*
2. Nitric acid, 10% (v/v). Add 100 mL conc. $HNO_3$ to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% $H_2O_2$ (w/w), reagent grade.*
4. Calibration stock solution, 1000 µg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable≥ one year.
5. Air, compressed, filtered.
6. Acetylene
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: Cellulose ester filter, 0.8-µm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140°C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

**SPECIAL PRECAUTIONS:** Concentrated nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 200 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

**SAMPLE PREPARATION:**

NOTE 1: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

NOTE 2: The Appendix gives a microwave digestion procedure which may be necessary for complete recovery of lead from some matrices, especially epoxy-based paint.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. $HNO_3$, and 1 mL 30% $H_2O_2$ and cover with a watchglass. Start reagent blanks at this step.
   NOTE: If $PbO_2$ is not present in the sample, the 30% $H_2O_2$ need not be added [2,4].
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Repeat two more times using 2 mL conc. $HNO_3$ and 1 mL 30% $H_2O_2$ each time.
7. Heat on 140 °C hotplate until ca. 0.5 mL liquid remains.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% $HNO_3$. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. $HNO_3$.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M $Na_2EDTA$ to each flask before dilution to volume: $CO_3^{2-}$, $PO_4^{3-}$, $I^-$, $F^-$, $CH_3COO^-$. If $Ca^{2+}$ or $SO_4^{2-}$ are present in 10-fold or greater excess, make all standards and samples 1% (w/w) in La[3].

**CALIBRATION AND QUALITY CONTROL:**

11. Prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb (2.5 to 200 µg Pb per sample).
    a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% $HNO_3$. Store the working standards in polyethylene bottles and prepare fresh weekly.
    b. Analyze the working standards together with the blanks and samples (steps 14 and 15).
    c. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
12. Aspirate a standard for every 10 samples to check for instrument drift.
13. Check recoveries with at least one spiked media blank per 10 samples. Use method of standard additions occasionally to check for interferences.

**MEASUREMENT:**

14. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [8]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D$_2$ or $H_2$ continuum, or Zeeman background correction mandatory at that wavelength.
15. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% $HNO_3$, reanalyze, and apply the appropriate dilution factor in the calculations.

**CALCULATIONS:**

16. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, $C_s$, and average media blank, $C_b$, from the calibration graph.
17. Using the solution volumes (mL) of the sample, $V_s$, and media blanks, $V_b$, calculate the concentration, C (mg/m$^3$), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

NOTE: µg/mL ≡ mg/m

**EVALUATION OF METHOD:**

Method S341 [9] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m$^3$ for a 180-L air sample, using generated atmospheres of lead nitrate [1]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-m mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the following results [2,4]:

| Species | Digestion Method | Analytical Recovery, % |
|---|---|---|
| Pb metal | $HNO_3$ only | 92 ± 4 |
| Pb metal | $HNO_3 + H_2O_2$ | 103 ± 3 |
| PbO | $HNO_3$ only | 93 ± 4 |
| PbS | $HNO_3$ only | 93 ± 5 |
| $PbO_2$ | $HNO_3$ only | 82 ± 3 |
| $PbO_2$ | $HNO_3 + H_2O_2$ | 100 ± 1 |
| Pb in paint* | $HNO_3$ only | 95 ± 6 |
| Pb in paint* | $HNO_3 + H_2O_2$ | 95 ± 6 |

*Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 µm [2]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was 97 ± 2%. Overall precision, $\hat{S}_{rT}$, was 0.072 for lead nitrate aerosol [1,9] and 0.068 for Pb fume [2,4].

**REFERENCES:**


[1] Documentationof the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[2] Heavy Metal Aerosols: Collection and Dissolution Efficiencies, Final Report of NIOSH Contract 210-79-0058, W. F. Gutknecht, M. H. Ranade, P. M. Grohse, A. Damle, and D. O'Neal, Research Triangle Institute; available as Order No. PB 83-106740 from NTIS, Springfield, VA 22161 (1981).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1979).

[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, S341 (revised 3/25/81), U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 102, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[6] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Lead (Revised Criteria), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-158 (1978).

[7] NIOSH Manual of Analytical Methods, 2nd ed., P&CAM 191.

[8] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).

[9] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S341, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[10] DataChem Laboratories in-house procedure for microwave sample digestion.

[11] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Ed; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, SW-846 (1986).

[12] Kingston, H.M. and L.B. Jassie, "Safety Guidelines for Microwave Systems in the Analytical Laboratory." Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, (1988).

[13] 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water; ASTM, Philadelphia, PA, D1193 – 77 (1985).

[14] Introduction to Microwave Sample Preparation: Theory and Practice; Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington DC (1988).

[15] Kingston, H.M. EPA IAG #DW1-393254-01-0 January 1 – March 31, 1988, Quarterly Report.

[16] Binstock, D.A., Yeager, W.M., Grohse, P.M. and Gaskill, A. Validation of a Method for Determining Elements in Solid Waste by Microwave Digestion, Research Triangle Institute Technical Report Draft, RTI Project Number 321U-3579-24, prepared for the Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460 (November, 1989).


**METHOD REVISED BY:**

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James B. Perkins, David L. Wheeler, and Keith Nicholson, Ph.D., DataChem Laboratories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

## APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption(HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material[11-16]

1. Microwave apparatus requirements
   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 $cm^2$ piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.
   c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.
   d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six,

or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180 °C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180 °C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in the following table.

**PROGRAM VARIABLES FOR PAINT CHIPS SAMPLE DIGESTION WITH NITRIC ACID**

| Stage | (1) | (2) | (3) |
|---|---|---|---|
| Power | 90% | 90% | 0% |
| Pressure, psi | 50 | 100 | 0 |
| Run Time, min | 10:00 | 20:00 | 05:00 |
| Time @ P, min | 05:00 | 15:00 | 00:00 |
| Temperature | 180°C | 180°C | 0°C |
| Fan Speed | 100% | 100% | 100% |

| | |
|---|---|
| Number of Vessels: | 12 |
| Liquid Volume per Vessel: | 5 mL |
| Sample Weight: | 0.1 g |

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

**Settling:** Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

**Filtering:** The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.

# GENERAL FIELD SAMPLING GUIDELINES

SOP#: 2001
DATE: 08/11/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to provide general field sampling guidelines that will assist REAC personnel in choosing sampling strategies, location, and frequency for proper assessment of site characteristics. This SOP is applicable to all field activities that involve sampling.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Sampling is the selection of a representative portion of a larger population, universe, or body. Through examination of a sample, the characteristics of the larger body from which the sample was drawn can be inferred. In this manner, sampling can be a valuable tool for determining the presence, type, and extent of contamination by hazardous substances in the environment.

The primary objective of all sampling activities is to characterize a hazardous waste site accurately so that its impact on human health and the environment can be properly evaluated. It is only through sampling and analysis that site hazards can be measured and the job of cleanup and restoration can be accomplished effectively with minimal risk. The sampling itself must be conducted so that every sample collected retains its original physical form and chemical composition. In this way, sample integrity is insured, quality assurance standards are maintained, and the sample can accurately represent the larger body of material under investigation.

The extent to which valid inferences can be drawn from a sample depends on the degree to which the sampling effort conforms to the project's objectives. For example, as few as one sample may produce adequate, technically valid data to address the project's objectives. Meeting the project's objectives requires thorough planning of sampling activities, and implementation of the most appropriate sampling and analytical procedures. These issues will be discussed in this procedure.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample to be collected, and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest. Sample preservation, containers, handling, and storage for air and waste samples are discussed in the specific SOPs for air and waste sampling techniques.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

The nature of the object or materials being sampled may be a potential problem to the sampler. If a material is homogeneous, it will generally have a uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the sampler because of changes in the material over distance, both laterally and vertically.

Samples of hazardous materials may pose a safety threat to both field and laboratory personnel. Proper health and safety precautions should be implemented when handling this type of sample.

Environmental conditions, weather conditions, or non-target chemicals may cause problems and/or interferences when performing sampling activities or when sampling for a specific parameter. Refer to the specific SOPs for sampling techniques.

## 5.0 EQUIPMENT/APPARATUS

The equipment/apparatus required to collect samples must be determined on a site specific basis. Due to the wide variety of sampling equipment available, refer to the specific SOPs for sampling techniques which include lists of the equipment/apparatus required for sampling.

## 6.0 REAGENTS

Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

## 7.0 PROCEDURE

### 7.1 Types of Samples

In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample.

Environmental samples are those collected from streams, ponds, lakes, wells, and are off-site samples that are not expected to be contaminated with hazardous materials. They usually do not require the special handling procedures typically used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples.

Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, or areas previously identified as contaminated, and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling and shipping any wastes believed to be concentrated regardless of the degree.

The importance of making the distinction between environmental and hazardous samples is two-fold:

(1) Personnel safety requirements: Any sample thought to contain enough hazardous materials to pose a safety threat should be designated as hazardous and handled in a manner which ensures the safety of both field and laboratory personnel.

(2) Transportation requirements: Hazardous samples must be packaged, labeled, and shipped according to the International Air Transport Association (IATA) Dangerous Goods Regulations or Department of Transportation (DOT) regulations and U.S. EPA guidelines.

### 7.2 Sample Collection Techniques

In general, two basic types of sample collection techniques are recognized, both of which can be used for either environmental or hazardous samples.

Grab Samples

A grab sample is defined as a discrete aliquot representative of a specific location at a given point in time. The sample is collected all at once at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials being sampled. In general, as sources vary over time and distance, the representativeness of grab samples will decrease.

Composite Samples

Composites are nondiscrete samples composed of more than one specific aliquot collected at various sampling locations and/or different points in time. Analysis of this type of sample produces an average value and can in certain instances be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits.

Compositing is often used for environmental samples and may be used for hazardous samples under certain conditions. For example, compositing of hazardous waste is often performed after compatibility tests have

been completed to determine an average value over a number of different locations (group of drums). This procedure generates data that can be useful by providing an average concentration within a number of units, can serve to keep analytical costs down, and can provide information useful to transporters and waste disposal operations.

For sampling situations involving hazardous wastes, grab sampling techniques are generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing.

## 7.3 Types of Sampling Strategies

The number of samples that should be collected and analyzed depends on the objective of the investigation. There are three basic sampling strategies: random, systematic, and judgmental sampling.

Random sampling involves collection of samples in a nonsystematic fashion from the entire site or a specific portion of a site. Systematic sampling involves collection of samples based on a grid or a pattern which has been previously established. When judgmental sampling is performed, samples are collected only from the portion(s) of the site most likely to be contaminated. Often, a combination of these strategies is the best approach depending on the type of the suspected/known contamination, the uniformity and size of the site, the level/type of information desired, etc.

## 7.4 QA Work Plans (QAWP)

A QAWP is required when it becomes evident that a field investigation is necessary. It should be initiated in conjunction with, or immediately following, notification of the field investigation. This plan should be clear and concise and should detail the following basic components, with regard to sampling activities:

- Objective and purpose of the investigation.
- Basis upon which data will be evaluated.
- Information known about the site including location, type and size of the facility, and length of operations/abandonment.
- Type and volume of contaminated material, contaminants of concern (including concentration), and basis of the information/data.
- Technical approach including media/matrix to be sampled, sampling equipment to be used, sample equipment decontamination (if necessary), sampling design and rationale, and SOPs or description of the procedure to be implemented.
- Project management and reporting, schedule, project organization and responsibilities, manpower and cost projections, and required deliverables.
- QA objectives and protocols including tables summarizing field sampling and QA/QC analysis and objectives.

Note that this list of QAWP components is not all-inclusive and that additional elements may be added or altered depending on the specific requirements of the field investigation. It should also be recognized that although a detailed QAWP is quite important, it may be impractical in some instances. Emergency responses and accidental spills are prime examples of such instances where time might prohibit the development of site-specific QAWPs prior to field activities. In such cases, investigators would have to rely on general guidelines and personal judgment, and the sampling or response plans might simply be a strategy based on preliminary information and finalized on site. In any event, a plan of action should be developed, no matter how concise or informal, to aid investigators in maintaining a logical and consistent order to the implementation of their task.

## 7.5 Legal Implications

The data derived from sampling activities are often introduced as critical evidence during litigation of a hazardous waste site cleanup. Legal issues in which sampling data are important may include cleanup cost recovery, identification of pollution sources and responsible parties, and technical validation of remedial design methodologies. Because of the potential for involvement in legal actions, strict adherence to technical and administrative SOPs is essential during both the development and implementation of sampling activities.

Technically valid sampling begins with thorough planning and continues through the sample collection and analytical procedures. Administrative requirements involve thorough, accurate

documentation of all sampling activities. Documentation requirements include maintenance of a chain of custody, as well as accurate records of field activities and analytical instructions. Failure to observe these procedures fully and consistently may result in data that are questionable, invalid and non-defensible in court, and the consequent loss of enforcement proceedings.

## 8.0 CALCULATIONS

Refer to the specific SOPs for any calculations which are associated with sampling techniques.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

Refer to the specific SOPs for the type and frequency of QA/QC samples to be analyzed, the acceptance criteria for the QA/QC samples, and any other QA/QC activities which are associated with sampling techniques.

## 10.0 DATA VALIDATION

Refer to the specific SOPs for data validation activities that are associated with sampling techniques.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety procedures.

# SAMPLING EQUIPMENT DECONTAMINATION

SOP#: 2006
DATE: 08/11/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to provide a description of the methods used for preventing, minimizing, or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during hazardous waste operations as per 29 Code of Federal Regulations (CFR) 1910.120. This SOP does not address personnel decontamination.

These are standard (i.e. typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitation, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Removing or neutralizing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances.

Gross contamination can be removed by physical decontamination procedures. These abrasive and non-abrasive methods include the use of brushes, air and wet blasting, and high and low pressure water cleaning.

The first step, a soap and water wash, removes all visible particulate matter and residual oils and grease. This may be preceded by a steam or high pressure water wash to facilitate residuals removal. The second step involves a tap water rinse and a distilled/deionized water rinse to remove the detergent. An acid rinse provides a low pH media for trace metals removal and is included in the decontamination process if metal samples are to be collected. It is followed by another distilled/deionized water rinse. If sample analysis does not include metals, the acid rinse step can be omitted. Next, a high purity solvent rinse is performed for trace organics removal if organics are a concern at the site. Typical solvents used for removal of organic contaminants include acetone, hexane, or water. Acetone is typically chosen because it is an excellent solvent, miscible in water, and not a target analyte on the Priority Pollutant List. If acetone is known to be a contaminant of concern at a given site or if Target Compound List analysis (which includes acetone) is to be performed, another solvent may be substituted. The solvent must be allowed to evaporate completely and then a final distilled/deionized water rinse is performed. This rinse removes any residual traces of the solvent.

The decontamination procedure described above may be summarized as follows:

1. Physical removal
2. Non-phosphate detergent wash
3. Tap water rinse
4. Distilled/deionized water rinse
5. 10% nitric acid rinse
6. Distilled/deionized water rinse
7. Solvent rinse (pesticide grade)
8. Air dry
9. Distilled/deionized water rinse

If a particular contaminant fraction is not present at the site, the nine (9) step decontamination procedure specified above may be modified for site specificity. For example, the nitric acid rinse may be eliminated if metals are not of concern at a site. Similarly, the solvent rinse may be eliminated if organics are not of

concern at a site. Modifications to the standard procedure should be documented in the site specific work plan or subsequent report.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample to be collected and the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix being sampled and the parameter(s) of interest.

More specifically, sample collection and analysis of decontamination waste may be required before beginning proper disposal of decontamination liquids and solids generated at a site. This should be determined prior to initiation of site activities.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- The use of distilled/deionized water commonly available from commercial vendors may be acceptable for decontamination of sampling equipment provided that it has been verified by laboratory analysis to be analyte free (specifically for the contaminants of concern).
- The use of an untreated potable water supply is not an acceptable substitute for tap water. Tap water may be used from any municipal or industrial water treatment system.
- If acids or solvents are utilized in decontamination they raise health and safety, and waste disposal concerns.
- Damage can be incurred by acid and solvent washing of complex and sophisticated sampling equipment.

## 5.0 EQUIPMENT/APPARATUS

Decontamination equipment, materials, and supplies are generally selected based on availability. Other considerations include the ease of decontaminating or disposing of the equipment. Most equipment and supplies can be easily procured. For example, soft-bristle scrub brushes or long-handled bottle brushes can be used to remove contaminants. Large galvanized wash tubs, stock tanks, or buckets can hold wash and rinse solutions. Children's wading pools can also be used. Large plastic garbage cans or other similar containers lined with plastic bags can help segregate contaminated equipment. Contaminated liquid can be stored temporarily in metal or plastic cans or drums.

The following standard materials and equipment are recommended for decontamination activities:

### 5.1 Decontamination Solutions

- Non-phosphate detergent
- Selected solvents (acetone, hexane, nitric acid, etc.)
- Tap water
- Distilled or deionized water

### 5.2 Decontamination Tools/Supplies

- Long and short handled brushes
- Bottle brushes
- Drop cloth/plastic sheeting
- Paper towels
- Plastic or galvanized tubs or buckets
- Pressurized sprayers ($H_2O$)
- Solvent sprayers
- Aluminum foil

### 5.3 Health and Safety Equipment

Appropriate personal protective equipment (i.e., safety glasses or splash shield, appropriate gloves, aprons or coveralls, respirator, emergency eye wash)

### 5.4 Waste Disposal

- Trash bags
- Trash containers
- 55-gallon drums
- Metal/plastic buckets/containers for storage and disposal of decontamination solutions

## 6.0 REAGENTS

There are no reagents used in this procedure aside from the actual decontamination solutions. Table 1 (Appendix A) lists solvent rinses which may be required for elimination of particular chemicals. In

general, the following solvents are typically utilized for decontamination purposes:

- 10% nitric acid is typically used for inorganic compounds such as metals. An acid rinse may not be required if inorganics are not a contaminant of concern.
- Acetone (pesticide grade)[1]
- Hexane (pesticide grade)[1]
- Methanol[1]

[1] - Only if sample is to be analyzed for organics.

## 7.0 PROCEDURES

As part of the health and safety plan, a decontamination plan should be developed and reviewed. The decontamination line should be set up before any personnel or equipment enter the areas of potential exposure. The equipment decontamination plan should include:

- The number, location, and layout of decontamination stations.
- Decontamination equipment needed.
- Appropriate decontamination methods.
- Methods for disposal of contaminated clothing, equipment, and solutions.
- Procedures can be established to minimize the potential for contamination. This may include: (1) work practices that minimize contact with potential contaminants; (2) using remote sampling techniques; (3) covering monitoring and sampling equipment with plastic, aluminum foil, or other protective material; (4) watering down dusty areas; (5) avoiding laying down equipment in areas of obvious contamination; and (6) use of disposable sampling equipment.

### 7.1 Decontamination Methods

All samples and equipment leaving the contaminated area of a site must be decontaminated to remove any contamination that may have adhered to equipment. Various decontamination methods will remove contaminants by: (1) flushing or other physical action, or (2) chemical complexing to inactivate contaminants by neutralization, chemical reaction, disinfection, or sterilization.

Physical decontamination techniques can be grouped into two categories: abrasive methods and non-abrasive methods, as follows:

#### 7.1.1 Abrasive Cleaning Methods

Abrasive cleaning methods work by rubbing and wearing away the top layer of the surface containing the contaminant. The mechanical abrasive cleaning methods are most commonly used at hazardous waste sites. The following abrasive methods are available:

Mechanical

Mechanical methods of decontamination include using metal or nylon brushes. The amount and type of contaminants removed will vary with the hardness of bristles, length of time brushed, degree of brush contact, degree of contamination, nature of the surface being cleaned, and degree of contaminant adherence to the surface.

Air Blasting

Air blasting equipment uses compressed air to force abrasive material through a nozzle at high velocities. The distance between nozzle and surface cleaned, air pressure, time of application, and angle at which the abrasive strikes the surface will dictate cleaning efficiency. Disadvantages of this method are the inability to control the amount of material removed and the large amount of waste generated.

Wet Blasting

Wet blast cleaning involves use of a suspended fine abrasive. The abrasive/water mixture is delivered by compressed air to the contaminated area. By using a very fine abrasive, the amount of materials removed can be carefully controlled.

#### 7.1.2 Non-Abrasive Cleaning Methods

Non-abrasive cleaning methods work by forcing the contaminant off a surface with pressure. In general, the equipment surface is not removed using non-abrasive methods.

Low-Pressure Water

This method consists of a container which is filled with water. The user pumps air out of the container to create a vacuum. A slender nozzle and hose allow the user to spray in hard-to-reach places.

High-Pressure Water

This method consists of a high-pressure pump, an operator controlled directional nozzle, and a high-pressure hose. Operating pressure usually ranges from 340 to 680 atmospheres (atm) and flow rates usually range from 20 to 140 liters per minute.

Ultra-High-Pressure Water

This system produces a water jet that is pressured from 1,000 to 4,000 atmospheres. This ultra-high-pressure spray can remove tightly-adhered surface films. The water velocity ranges from 500 meters/second (m/s) (1,000 atm) to 900 m/s (4,000 atm). Additives can be used to enhance the cleaning action.

Rinsing

Contaminants are removed by rinsing through dilution, physical attraction, and solubilization.

Damp Cloth Removal

In some instances, due to sensitive, non-waterproof equipment or due to the unlikelihood of equipment being contaminated, it is not necessary to conduct an extensive decontamination procedure. For example, air sampling pumps hooked on a fence, placed on a drum, or wrapped in plastic bags are not likely to become heavily contaminated. A damp cloth should be used to wipe off contaminants which may have adhered to equipment through airborne contaminants or from surfaces upon which the equipment was set.

Disinfection/Sterilization

Disinfectants are a practical means of inactivating infectious agents. Unfortunately, standard sterilization methods are impractical for large equipment. This method of decontamination is typically performed off-site.

## 7.2 Field Sampling Equipment Decontamination Procedures

The decontamination line is setup so that the first station is used to clean the most contaminated item. It progresses to the last station where the least contaminated item is cleaned. The spread of contaminants is further reduced by separating each decontamination station by a minimum of three (3) feet. Ideally, the contamination should decrease as the equipment progresses from one station to another farther along in the line.

A site is typically divided up into the following boundaries: Hot Zone or Exclusion Zone (EZ), the Contamination Reduction Zone (CRZ), and the Support or Safe Zone (SZ). The decontamination line should be setup in the Contamination Reduction Corridor (CRC) which is in the CRZ. Figure 1 (Appendix B) shows a typical contaminant reduction zone layout. The CRC controls access into and out of the exclusion zone and confines decontamination activities to a limited area. The CRC boundaries should be conspicuously marked. The far end is the hotline, the boundary between the exclusion zone and the contamination reduction zone. The size of the decontamination corridor depends on the number of stations in the decontamination process, overall dimensions of the work zones, and amount of space available at the site. Whenever possible, it should be a straight line.

Anyone in the CRC should be wearing the level of protection designated for the decontamination crew. Another corridor may be required for the entry and exit of heavy equipment. Sampling and monitoring equipment and sampling supplies are all maintained outside of the CRC. Personnel don their equipment away from the CRC and enter the exclusion zone through a separate access control point at the hotline. One person (or more) dedicated to decontaminating equipment is recommended.

### 7.2.1 Decontamination Setup

Starting with the most contaminated station, the decontamination setup should be as follows:

Station 1: Segregate Equipment Drop

Place plastic sheeting on the ground (Figure 2, Appendix B). Size will depend on amount of

equipment to be decontaminated. Provide containers lined with plastic if equipment is to be segregated. Segregation may be required if sensitive equipment or mildly contaminated equipment is used at the same time as equipment which is likely to be heavily contaminated.

Station 2: Physical Removal With A High-Pressure Washer (Optional)

As indicated in 7.1.2, a high-pressure wash may be required for compounds which are difficult to remove by washing with brushes. The elevated temperature of the water from the high-pressure washers is excellent at removing greasy/oily compounds. High pressure washers require water and electricity.

A decontamination pad may be required for the high-pressure wash area. An example of a wash pad may consist of an approximately 1 1/2 foot-deep basin lined with plastic sheeting and sloped to a sump at one corner. A layer of sand can be placed over the plastic and the basin is filled with gravel or shell. The sump is also lined with visqueen and a barrel is placed in the hole to prevent collapse. A sump pump is used to remove the water from the sump for transfer into a drum.

Typically heavy machinery is decontaminated at the end of the day unless site sampling requires that the machinery be decontaminated frequently. A separate decontamination pad may be required for heavy equipment.

Station 3: Physical Removal With Brushes And A Wash Basin

Prior to setting up Station 3, place plastic sheeting on the ground to cover areas under Station 3 through Station 10.
Fill a wash basin, a large bucket, or child's swimming pool with non-phosphate detergent and tap water. Several bottle and bristle brushes to physically remove contamination should be dedicated to this station. Approximately 10 - 50 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 4: Water Basin

Fill a wash basin, a large bucket, or child's swimming pool with tap water. Several bottle and bristle brushes should be dedicated to this station. Approximately 10-50 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 5: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to contain the water during the rinsing process. Approximately 10-20 gallons of water may be required initially depending upon the amount of equipment to decontaminate and the amount of gross contamination.

Station 6: Nitric Acid Sprayers

Fill a spray bottle with 10% nitric acid. An acid rinse may not be required if inorganics are not a contaminant of concern. The amount of acid will depend on the amount of equipment to be decontaminated. Provide a 5-gallon bucket or basin to collect acid during the rinsing process.

Station 7: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 8: Organic Solvent Sprayers

Fill a spray bottle with an organic solvent. After each solvent rinse, the equipment should be rinsed with distilled/deionized water and air dried. Amount of solvent will depend on the amount of equipment to decontaminate. Provide a 5-gallon bucket or basin to collect the solvent during the rinsing process.

Solvent rinses may not be required unless organics are a contaminant of concern, and may be eliminated from the station sequence.

Station 9: Low-Pressure Sprayers

Fill a low-pressure sprayer with distilled/deionized water. Provide a 5-gallon bucket or basin to collect water during the rinsate process.

Station 10: Clean Equipment Drop

Lay a clean piece of plastic sheeting over the bottom

plastic layer. This will allow easy removal of the plastic in the event that it becomes dirty. Provide aluminum foil, plastic, or other protective material to wrap clean equipment.

### 7.2.2 Decontamination Procedures

Station 1: Segregate Equipment Drop

Deposit equipment used on-site (i.e., tools, sampling devices and containers, monitoring instruments radios, clipboards, etc.) on the plastic drop cloth/sheet or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross contamination. Loose leaf sampling data sheets or maps can be placed in plastic zip lock bags if contamination is evident.

Station 2: Physical Removal With A High-Pressure Washer (Optional)

Use high pressure wash on grossly contaminated equipment. Do not use high- pressure wash on sensitive or non-waterproof equipment.

Station 3: Physical Removal With Brushes And A Wash Basin

Scrub equipment with soap and water using bottle and bristle brushes. Only sensitive equipment (i.e., radios, air monitoring and sampling equipment) which is waterproof should be washed. Equipment which is not waterproof should have plastic bags removed and wiped down with a damp cloth. Acids and organic rinses may also ruin sensitive equipment. Consult the manufacturers for recommended decontamination solutions.

Station 4: Equipment Rinse

Wash soap off of equipment with water by immersing the equipment in the water while brushing. Repeat as many times as necessary.

Station 5: Low-Pressure Rinse

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 6: Nitric Acid Sprayers ( required only if metals are a contaminant of concern)

Using a spray bottle rinse sampling equipment with nitric acid. Begin spraying (inside and outside) at one end of the equipment allowing the acid to drip to the other end into a 5-gallon bucket. A rinsate blank may be required at this station. Refer to Section 9.

Station 7: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure sprayer.

Station 8: Organic Solvent Sprayers

Rinse sampling equipment with a solvent. Begin spraying (inside and outside) at one end of the equipment allowing the solvent to drip to the other end into a 5-gallon bucket. Allow the solvent to evaporate from the equipment before going to the next station. A QC rinsate sample may be required at this station.

Station 9: Low-Pressure Sprayers

Rinse sampling equipment with distilled/deionized water with a low-pressure washer.

Station 10 : Clean Equipment Drop

Lay clean equipment on plastic sheeting. Once air dried, wrap sampling equipment with aluminum foil, plastic, or other protective material.

### 7.2.3 Post Decontamination Procedures

1. Collect high-pressure pad and heavy equipment decontamination area liquid and waste and store in appropriate drum or container. A sump pump can aid in the collection process. Refer to the Department of Transportation (DOT) requirements for appropriate containers based on the contaminant of concern.

2. Collect high-pressure pad and heavy equipment decontamination area solid waste and store in appropriate drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

3. Empty soap and water liquid wastes from basins and buckets and store in appropriate

drum or container. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

4. Empty acid rinse waste and place in appropriate container or neutralize with a base and place in appropriate drum. pH paper or an equivalent pH test is required for neutralization. Consult DOT requirements for appropriate drum for acid rinse waste.

5. Empty solvent rinse sprayer and solvent waste into an appropriate container. Consult DOT requirements for appropriate drum for solvent rinse waste.

6. Using low-pressure sprayers, rinse basins, and brushes. Place liquid generated from this process into the wash water rinse container.

7. Empty low-pressure sprayer water onto the ground.

8. Place all solid waste materials generated from the decontamination area (i.e., gloves and plastic sheeting, etc.) in an approved DOT drum. Refer to the DOT requirements for appropriate containers based on the contaminant of concern.

9. Write appropriate labels for waste and make arrangements for disposal. Consult DOT regulations for the appropriate label for each drum generated from the decontamination process.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITYASSURANCE/ QUALITY CONTROL

A rinsate blank is one specific type of quality control sample associated with the field decontamination process. This sample will provide information on the effectiveness of the decontamination process employed in the field.

Rinsate blanks are samples obtained by running analyte free water over decontaminated sampling equipment to test for residual contamination. The blank water is collected in sample containers for handling, shipment, and analysis. These samples are treated identical to samples collected that day. A rinsate blank is used to assess cross contamination brought about by improper decontamination procedures. Where dedicated sampling equipment is not utilized, collect one rinsate blank per day per type of sampling device samples to meet QA2 and QA3 objectives.

If sampling equipment requires the use of plastic tubing it should be disposed of as contaminated and replaced with clean tubing before additional sampling occurs.

## 10.0 DATA VALIDATION

Results of quality control samples will be evaluated for contamination. This information will be utilized to qualify the environmental sample results in accordance with the project's data quality objectives.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow OSHA, U.S. EPA, corporate, and other applicable health and safety procedures.

Decontamination can pose hazards under certain circumstances. Hazardous substances may be incompatible with decontamination materials. For example, the decontamination solution may react with contaminants to produce heat, explosion, or toxic products. Also, vapors from decontamination solutions may pose a direct health hazard to workers by inhalation, contact, fire, or explosion.

The decontamination solutions must be determined to be acceptable before use. Decontamination materials may degrade protective clothing or equipment; some solvents can permeate protective clothing. If decontamination materials do pose a health hazard, measures should be taken to protect personnel or substitutions should be made to eliminate the hazard. The choice of respiratory protection based on contaminants of concern from the site may not be appropriate for solvents used in the decontamination process.

Safety considerations should be addressed when using abrasive and non-abrasive decontamination

equipment. Maximum air pressure produced by abrasive equipment could cause physical injury. Displaced material requires control mechanisms.

Material generated from decontamination activities requires proper handling, storage, and disposal. Personal Protective Equipment may be required for these activities.

Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard (i.e., acetone, alcohol, and trisodiumphosphate).

In some jurisdictions, phosphate containing detergents (i.e., TSP) are banned.

## 12.0 REFERENCES


Field Sampling Procedures Manual, New Jersey Department of Environmental Protection, February, 1988.

A Compendium of Superfund Field Operations Methods, EPA 540/p-87/001.

Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual, USEPA Region IV, April 1, 1986.

Guidelines for the Selection of Chemical Protective Clothing, Volume 1, Third Edition, American Conference of Governmental Industrial Hygienists, Inc., February, 1987.

Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, NIOSH/OSHA/USCG/EPA, October, 1985.

# APPENDIX A

## Table

Table 1. Soluble Contaminants and Recommended Solvent Rinse

TABLE 1
Soluble Contaminants and Recommended Solvent Rinse

| SOLVENT[1] | EXAMPLES OF SOLVENTS | SOLUBLE CONTAMINANTS |
|---|---|---|
| Water | Deionized water<br>Tap water | Low-chain hydrocarbons<br>Inorganic compounds<br>Salts<br>Some organic acids and other polar compounds |
| Dilute Acids | Nitric acid<br>Acetic acid<br>Boric acid | Basic (caustic) compounds (e.g., amines and hydrazines) |
| Dilute Bases | Sodium bicarbonate (e.g., soap detergent) | Acidic compounds<br>Phenol<br>Thiols<br>Some nitro and sulfonic compounds |
| Organic Solvents [2] | Alcohols<br>Ethers<br>Ketones<br>Aromatics<br>Straight chain alkalines (e.g., hexane)<br>Common petroleum products (e.g., fuel, oil, kerosene) | Nonpolar compounds (e.g., some organic compounds) |
| Organic Solvent[2] | Hexane | PCBs |

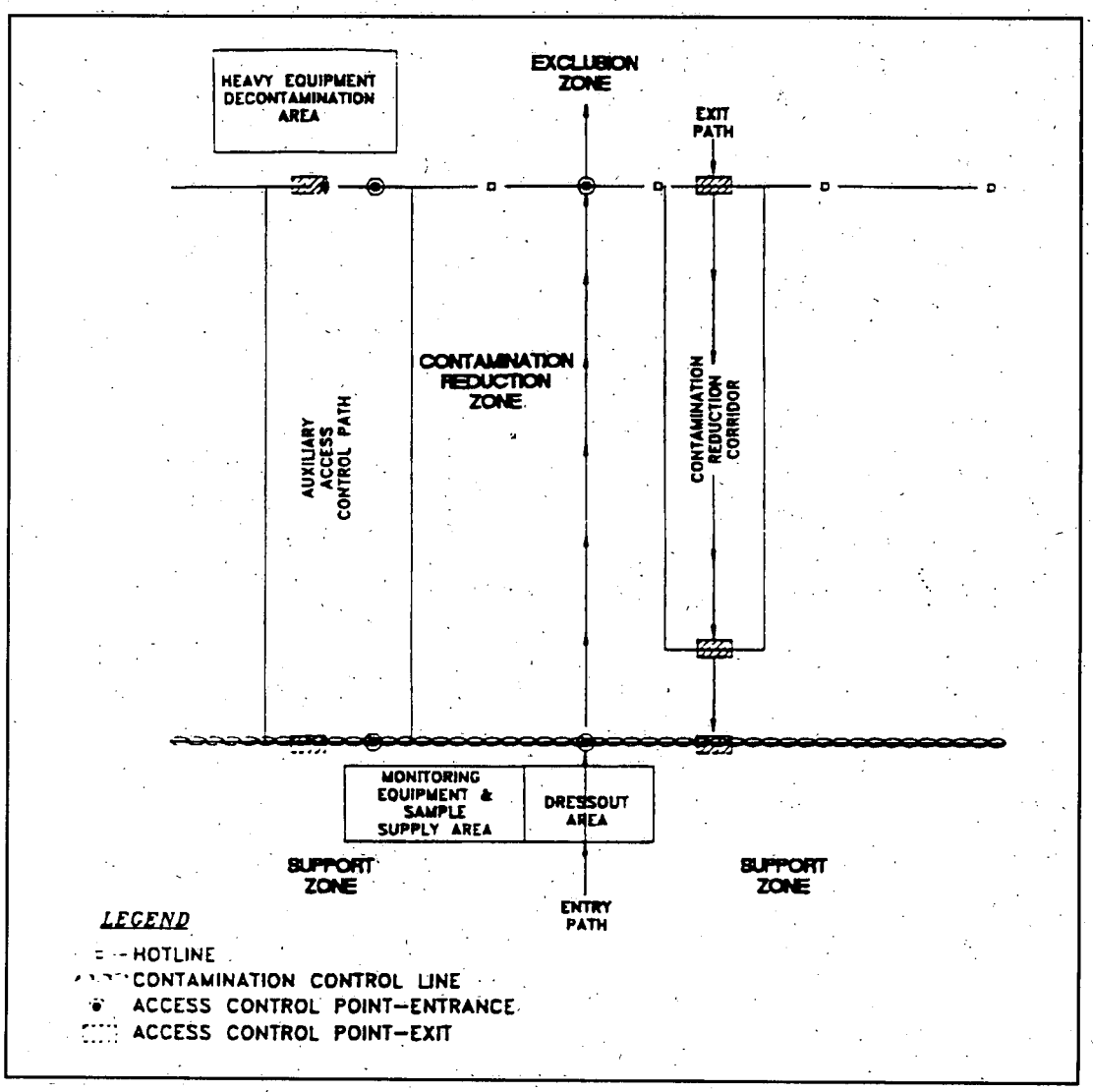
(1) - Material safety data sheets are required for all decontamination solvents or solutions as required by the Hazard Communication Standard

(2) - WARNING: Some organic solvents can permeate and/or degrade the protective clothing

# APPENDIX B

## Figures

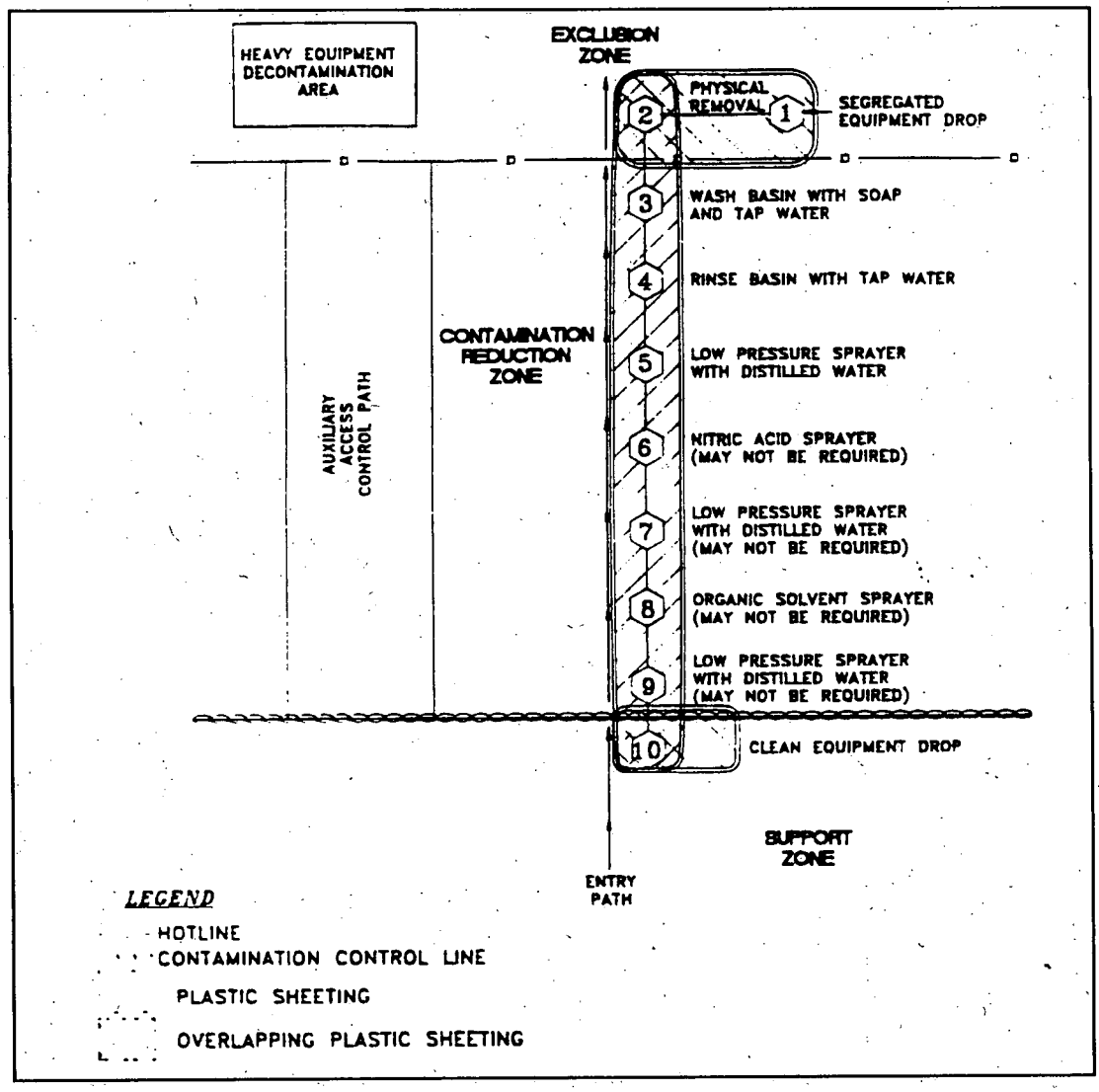
Figure 1. Contamination Reduction Zone Layout



# APPENDIX B (Cont'd.)

Figures

Figure 2. Decontamination Layout



# GROUNDWATER WELL SAMPLING

SOP#: 2007
DATE: 01/26/95
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

The objective of this standard operating procedure (SOP) is to provide general reference information on sampling of ground water wells. This guideline is primarily concerned with the collection of water samples from the saturated zone of the subsurface. Every effort must be made to ensure that the sample is representative of the particular zone of water being sampled. These procedures are designed to be used in conjunction with analyses for the most common types of ground water contaminants (e.g., volatile and semi-volatile organic compounds, pesticides, metals, biological parameters).

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

In order to obtain a representative groundwater sample for chemical analysis it is important to remove stagnant water in the well casing and the water immediately adjacent to the well before collection of the sample. This may be achieved with one of a number of instruments. The most common of these are the bailer, submersible pump, non-contact gas bladder pump, inertia pump and suction pump. At a minimum, three well volumes should be purged, if possible. Equipment must be decontaminated prior to use and between wells. Once purging is completed and the correct laboratory-cleaned sample containers have been prepared, sampling may proceed. Sampling may be conducted with any of the above instruments, and need not be the same as the device used for purging. Care should be taken when choosing the sampling device as some will affect the integrity of the sample. Sampling should occur in a progression from the least to most contaminated well, if this information is known.

The growing concern over the past several years over low levels of volatile organic compounds in water supplies has led to the development of highly sophisticated analytical methods that can provide detection limits at part per trillion levels. While the laboratory methods are extremely sensitive, well controlled and quality assured, they cannot compensate for a poorly collected sample. The collection of a sample should be as sensitive, highly developed and quality assured as the analytical procedures.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The type of analysis for which a sample is being collected determines the type of bottle, preservative, holding time, and filtering requirements. Samples should be collected directly from the sampling device into appropriate laboratory cleaned containers. Check that a Teflon liner is present in the cap, if required. Attach a sample identification label. Complete a field data sheet, a chain of custody form, and record all pertinent data in the site logbook.

Samples shall be appropriately preserved, labelled, logged, and placed in a cooler to be maintained at 4°C. Samples must be shipped well before the holding time is up and ideally should be shipped within 24 hours of sample collection. It is imperative that samples be shipped or delivered daily to the analytical laboratory in order to maximize the time available for the laboratory to perform the analyses. The bottles should be shipped with adequate packing and cooling to ensure that they arrive intact.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must remain to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

Treatment of the sample with sodium thiosulfate preservative is required only if there is residual chlorine in the water that could cause free radical chlorination and change the identity of the original contaminants. It should not be used if there is no chlorine in the water.

Holding time for volatiles analysis is seven days. It is imperative that the sample be shipped or delivered daily to the analytical laboratory. The bottles must be shipped on their sides to aid in maintaining the airtight seal during shipment, with adequate packing and cooling to ensure that they arrive intact.

For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies; field kit for chlorine, preservatives, Parafilm, foam sleeves and coolers. Due to the extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.

# 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

## 4.1 General

The primary goal in performing ground water sampling is to obtain a representative sample of the ground water body. Analysis can be compromised by field personnel in two primary ways: (1) taking an unrepresentative sample, or (2) by incorrect handling of the sample. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utilizing trained field personnel.

## 4.2 Purging

In a nonpumping well, there will be little or no vertical mixing of the water, and stratification will occur. The well water in the screened section will mix with the ground water due to normal flow patterns, but the well water above the screened section will remain isolated, become stagnant, and may lack the contaminants representative of the ground water. Persons sampling should realize that stagnant water may contain foreign material inadvertently or deliberately introduced from the surface, resulting in an unrepresentative sample. To safeguard against collecting nonrepresentative stagnant water, the following guidelines and techniques should be adhered to during sampling:

1. As a general rule, all monitor wells should be pumped or bailed prior to sampling. Purge water should be containerized on site or handled as specified in the site specific project plan. Evacuation of a minimum of one volume of water in the well casing, and preferably three to five volumes, is recommended for a representative sample. In a high-yielding ground water formation and where there is no stagnant water in the well above the screened section, evacuation prior to sample withdrawal is not as critical. However, in all cases where the monitoring data is to be used for enforcement actions, evacuation is recommended.

2. When purging with a pump (not a bailer), the pump should be set at the screened interval, or if the well is an open-rock well, it should be set at the same depth the sample will be collected. When sampling a screened well, the sample should also be collected from the same depth the pump was set at.

3. The well should be sampled as soon as possible after purging.

4. Analytical parameters typically dictate whether the sample should be collected through the purging device, or through a separate sampling instrument.

5. For wells that can be pumped or bailed to dryness with the equipment being used, the well should be evacuated and allowed to

recover prior to collecting a sample. If the recovery rate is fairly rapid and time allows, evacuation of more than one volume of water is preferred. If recovery is slow, sample the well upon recovery after one evacuation.

6. A non-representative sample can also result from excessive pre-pumping of the monitoring well. Stratification of the leachate concentration in the ground water formation may occur, or heavier-than-water compounds may sink to the lower portions of the aquifer. Excessive pumping can dilute or increase the contaminant concentrations from what is representative of the sampling point of interest.

## 4.3 Materials

Materials of construction for samplers and evacuation equipment (bladders, pump, bailers, tubing, etc.) should be limited to stainless steel, Teflon$^{R}$, and glass in areas where concentrations are expected to be at or near the detection limit. The tendency of organics to leach into and out of many materials make the selection of materials critical for trace analyses. The use of plastics, such as PVC or polyethylene, should be avoided when analyzing for organics. However, PVC may be used for evacuation equipment as it will not come in contact with the sample, and in highly contaminated wells, disposable equipment (i.e., polypropylene bailers) may be appropriate to avoid cross-contamination.

Materials of construction (bladders/ pumps, bailers, tubing, etc.) suitable for collecting and handling Volatile Organic Samples should be limited to stainless steel, Teflon and glass in areas which detection limit range concentrations are expected. The tendency of organics to leach into and out of many materials, make the selection of materials critical for these trace analyses. The use of plastics, e.g., PVC etc., should be avoided. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utlization of trained personnel.

## 4.4 Advantages/Disadvantages of Certain Equipment

### 4.4.1 Bailers

Advantages

- Only practical limitations on size and materials
- No power source needed
- Portable
- Inexpensive, so it can be dedicated and hung in a well, thereby reducing the chances of cross contamination
- Minimal outgassing of volatile organics while sample is in bailer
- Readily available
- Removes stagnant water first
- Rapid, simple method for removing small volumes of purge water

Disadvantages

- Time-consuming to flush a large well of stagnant water
- Transfer of sample may cause aeration
- Stoppers at the bottom of the bailer usually leak thus the bailer must be brought to the surface rapidly
- If the bailer is allowed to hit the bottom of the well boring, gravel can displace the ball valve not allowing the bailer to hold water

### 4.4.2 Submersible Pumps

Advantages

- Portable and can be transported to several wells
- Depending upon the size of the pump and the pumping depths, relatively high pumping rates are possible
- Generally very reliable and does not require priming

Disadvantages

- Potential for effects on analysis of trace organics
- Heavy and cumbersome to deal with, particularly in deeper wells
- Expensive
- Power source needed
- Sediment in water may cause problems with the pumps
- Impractical in low yielding or shallow wells

### 4.4.3 Non-Contact Gas Bladder Pumps

Advantages

- Maintains integrity of sample
- Easy to use
- Can sample from discrete locations within the monitor well

Disadvantages

- Difficulty in cleaning, though dedicated tubing and bladder may be used
- Only useful to about 100 feet
- Supply of gas for operation, gas bottles and/or compressors are often difficult to obtain and are cumbersome
- Relatively low pumping rates
- Requires air compressor or pressurized gas source and control box

### 4.4.4 Suction Pumps

Advantages

- Portable, inexpensive, and readily available

Disadvantages

- Restricted to areas with water levels within 20 to 25 feet of the ground surface
- Vacuum can cause loss of dissolved gasses and volatile organics
- Pump must be primed and vacuum is often difficult to maintain during initial stages of pumping

### 4.4.5 Inertia Pumps

Advantages

- Portable, inexpensive, and readily available
- Offers a rapid method for purging relatively shallow wells

Disadvantages

- Restricted to areas with water levels within 70 feet of the ground surface
- May be time consuming to purge wells with these manual pumps
- Labor intensive
- WaTerra pumps are only effective in 2-inch diameter wells

## 5.0 EQUIPMENT APPARATUS

## 5.1 Equipment Checklist

### 5.1.1 General

- Water level indicator
  - electric sounder
  - steel tape
  - transducer
  - reflection sounder
  - airline
- Depth sounder
- Appropriate keys for well cap locks
- Steel brush
- HNU or OVA (whichever is most appropriate)
- Logbook
- Calculator
- Field data sheets and samples labels

- Chain of custody records and seals
- Sample containers
- Engineer's rule
- Sharp knife (locking blade)
- Tool box (to include at least: screwdrivers, pliers, hacksaw, hammer, flashlight, adjustable wrench)
- Leather work gloves
- Appropriate Health & Safety gear
- 5-gallon pail
- Plastic sheeting
- Shipping containers
- Packing materials
- Bolt cutters
- Ziploc plastic bags
- Containers for evacuation liquids
- Decontamination solutions
- Tap water
- Non phosphate soap
- Several brushes
- Pails or tubs
- Aluminum foil
- Garden sprayer
- Preservatives
- Distilled or deionized water
- Fire extinguisher (if using a generator for your power source)

### 5.1.2 Bailers

- Clean, decontaminated bailers of appropriate size and construction material
- Nylon line, enough to dedicate to each well
- Teflon coated bailer wire
- Sharp knife
- Aluminum foil (to wrap clean bailers)
- Five gallon bucket

### 5.1.3 Submersible Pump

- Pump(s)
- Generator (110, 120, or 240 volt) or 12 volt battery if inaccessible to field vehicle - amp meter is useful
- 1" black PVC coil tubing - enough to dedicate to each well
- Hose clamps
- Safety cable
- Tool box supplement
  - pipe wrenches
  - wire strippers
  - electrical tape
  - heat shrink
  - hose connectors
  - Teflon tape
- Winch, pulley or hoist
- Gasoline for generator/gas can
- Flow meter with gate valve
- 1" nipples and various plumbing (i.e., pipe connectors)
- Control box (if necessary)

### 5.1.4 Non-Gas Contact Bladder Pump

- Non-gas contact bladder pump
- Compressor or nitrogen gas tank
- Batteries and charger
- Teflon tubing - enough to dedicate to each well
- Swagelock fitting
- Toolbox supplements - same as submersible pump
- Control box (if necessary)

### 5.1.5 Suction Pump

- Pump
- 1" black PVC coil tubing - enough to dedicate to each well
- Gasoline - if required
- Toolbox
- Plumbing fittings
- Flow meter with gate valve

### 5.1.6 Inertia Pump

- Pump assembly (WaTerra pump, piston pump)
- Five gallon bucket

## 6.0 REAGENTS

Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

## 7.0 PROCEDURE

### 7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed (i.e, diameter and depth of wells to be sampled).

2. Obtain necessary sampling and monitoring equipment, appropriate to type of contaminant being investigated. For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies; field kit for chlorine, preservatives, Parafilm, foam sleeves and coolers. Due to extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.

3. Decontaminate or preclean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Identify and mark all sampling locations.

### 7.2 Field Preparation

1. Start at the least contaminated well, if known.

2. Lay plastic sheeting around the well to minimize likelihood of contamination of equipment from soil adjacent to the well.

3. Remove locking well cap, note location, time of day, and date in field notebook or appropriate log form.

4. Remove well casing cap.

5. Screen headspace of well with an appropriate monitoring instrument to determine the presence of volatile organic compounds and record in site logbook.

6. Lower water level measuring device or equivalent (i.e., permanently installed transducers or airline) into well until water surface is encountered.

7. Measure distance from water surface to reference measuring point on well casing or protective barrier post and record in site logbook. Alternatively, if no reference point, note that water level measurement is from top of steel casing, top of PVC riser pipe, from ground surface, or some other position on the well head.

   If floating organics are of concern, this can be determined by measuring the water level with an oil/water interface probe which measures floating organics.

8. Measure total depth of well (at least twice to confirm measurement) and record in site logbook or on field data sheet.

9. Calculate the volume of water in the well and the volume to be purged using the calculations in Section 8.0.

10. Select the appropriate purging and sampling equipment.

11. If residual chlorine is suspected, use the Hach Field Test Kit for chlorine to determine if there is residual chlorine in the water to be sampled. If there is, treat the sample vial with a crystal of sodium thiosulfate prior to sample collection.

### 7.3 Purging

The amount of flushing a well receives prior to sample collection depends on the intent of the monitoring program as well as the hydrogeologic conditions. Programs where overall quality determination of water resources are involved may require long pumping periods to obtain a sample that is representative of a large volume of that aquifer. The pumped volume can be determined prior to sampling so that the sample is

a collected after a known volume of the water is evacuated from the aquifer, or the well can be pumped until the stabilization of parameters such as temperature, electrical conductance, pH, or turbidity has occurred.

However, monitoring for defining a contaminant plume requires a representative sample of a small volume of the aquifer. These circumstances require that the well be pumped enough to remove the stagnant water but not enough to induce flow from other areas. Generally, three well volumes are considered effective, or calculations can be made to determine, on the basis of the aquifer parameters and well dimensions, the appropriate volume to remove prior to sampling.

During purging, water level measurements may be taken regularly at 15-30 second intervals. This data may be used to compute aquifer transmissivity and other hydraulic characteristics. The following well evacuation devices are most commonly used. Other evacuation devices are available, but have been omitted in this discussion due to their limited use.

### 7.3.1 Bailers

Bailers are the simplest purging device used and have many advantages. They generally consist of a rigid length of tube, usually with a ball check-valve at the bottom. A line is used to lower the bailer into the well and retrieve a volume of water. The three most common types of bailer are PVC, Teflon, and stainless steel.

This manual method of purging is best suited to shallow or narrow diameter wells. For deep, larger diameter wells which require evacuation of large volumes of water, other mechanical devices may be more appropriate.

#### 7.3.1.1 Operation

Equipment needed will include a clean decontaminated bailer, Teflon or nylon line, a sharp knife, and plastic sheeting.

1. Determine the volume of water to be purged as described in 8.0, calculations.

2. Lay plastic sheeting around the well to prevent contamination of the bailer line with foreign materials.

3. Attach the line to the bailer and slowly lower until the bailer is completely submerged, being careful not to drop the bailer to the water, causing turbulence and the possible loss of volatile organic contaminants.

4. Pull bailer out ensuring that the line either falls onto a clean area of plastic sheeting or never touches the ground.

5. Empty the bailer into a pail until full to determine the number of bails necessary to achieve the required purge volume.

6. Thereafter, pour the water into a container and dispose of purge waters as specified in the site specific sampling plan.

### 7.3.2 Submersible Pumps

The use of submersible pumps for sample collection is permissible provided they are constructed of suitably noncontaminating materials. The chief drawback, however, is the difficulty avoiding cross-contamination between wells. Although some units can be disassembled easily to allow surfaces contacted by contaminants to be cleaned, field decontamination may be difficult and require solvents that can affect sample analysis. The use of submersible pumps in multiple well-sampling programs, therefore, should be carefully considered against other sampling mechanisms (bailers, bladder pumps). In most cases, a sample can be collected by bailer after purging with a submersible pump, however, submersible pumps may be the only practical sampling device for extremely deep wells (greater than 300 feet of water). Under those conditions, dedicated pump systems should be installed to eliminate the potential for cross-contamination of well samples.

Submersible pumps generally use one of two types of power supplies, either electric or compressed gas or air. Electric powered pumps can run off a 12 volt DC rechargeable battery, or a 110 or 220 volt AC power supply. Those units powered by compressed air normally use a small electric or gas-powered air compressor. They may also utilize compressed gas (i.e., nitrogen) from bottles. Different size pumps are available for different depth or diameter monitoring wells.

#### 7.3.2.1 Operation

1. Determine the volume of water to be purged as described in 8.0 Calculations.

2. Lay plastic sheeting around the well to prevent contamination of pumps, hoses or lines with foreign materials.

3. Assemble pump, hoses and safety cable, and lower the pump into the well. Make sure the pump is deep enough so all the water is not evacuated. (Running the pump without water may cause damage.)

4. Attach flow meter to the outlet hose to measure the volume of water purged.

5. Use a ground fault circuit interrupter (GFCI) or ground the generator to avoid possible electric shock.

6. Attach power supply, and purge the well until the specified volume of water has been evacuated (or until field parameters, such as temperature, pH, conductivity, etc, have stabilized). Do not allow the pump to run dry. If the pumping rate exceeds the well recharge rate, lower the pump further into the well, and continue pumping.

7. Collect and dispose of purge waters as specified in the site specific sampling plan.

### 7.3.3 Non-Contact Gas Bladder Pumps

For this procedure, an all stainless-steel and Teflon Middleburg-squeeze bladder pump (e.g., IEA, TIMCO, Well Wizard, Geoguard, and others) is used to provide the least amount of material interference to the sample (Barcelona, 1985). Water comes into contact with the inside of the bladder (Teflon) and the sample tubing, also Teflon, that may be dedicated to each well. Some wells may have permanently installed bladder pumps, (i.e., Well Wizard, Geoguard), that will be used to sample for all parameters.

#### 7.3.3.1 Operation

1. Assemble Teflon tubing, pump and charged control box.

2. Procedure for purging with a bladder pump is the same as for a submersible pump (Section 7.3.2.1).

3. Be sure to adjust flow rate to prevent violent jolting of the hose as sample is drawn in.

### 7.3.4 Suction Pumps

There are many different types of suction pumps. They include: centrifugal, peristaltic and diaphragm. Diaphragm pumps can be used for well evacuation at a fast pumping rate and sampling at a low pumping rate. The peristaltic pump is a low volume pump that uses rollers to squeeze the flexible tubing thereby creating suction. This tubing can be dedicated to a well to prevent cross contamination. Peristaltic pumps, however, require a power source.

#### 7.3.4.1 Operation

1. Assembly of the pump, tubing, and power source if necessary.

2. Procedure for purging with a suction pump is exactly the same as for a submersible pump (Section 7.3.2.1).

### 7.3.5 Inertia Pumps

Inertia pumps such as the WaTerra pump and piston pump, are manually operated. They are most appropriate to use when wells are too deep to bail by hand, or too shallow or narrow (or inaccessible) to warrant an automatic (submersible, etc.) pump. These pumps are made of plastic and may be either decontaminated or discarded.

#### 7.3.5.1 Operation

1. Determine the volume of water to be purged as described in 8.0, Calculations.

2. Lay plastic sheeting around the well to prevent contamination of pumps or hoses with foreign materials.

3. Assemble pump and lower to the appropriate depth in the well.

4. Begin pumping manually, discharging water into a 5 gallon bucket (or other graduated vessel). Purge until specified volume of water has been evacuated (or until field parameters such as temperature, pH,

conductivity, etc. have stabilized).

5. Collect and dispose of purge waters as specified in the site specific project plan.

## 7.4 Sampling

Sample withdrawal methods require the use of pumps, compressed air, bailers, and samplers. Ideally, purging and sample withdrawal equipment should be completely inert, economical to manufacture, easily cleaned, sterilized, reusable, able to operate at remote sites in the absence of power resources, and capable of delivering variable rates for sample collection.

There are several factors to take into consideration when choosing a sampling device. Care should be taken when reviewing the advantages or disadvantages of any one device. It may be appropriate to use a different device to sample than that which was used to purge. The most common example of this is the use of a submersible pump to purge and a bailer to sample.

### 7.4.1 Bailers

The positive-displacement volatile sampling bailer is perhaps the most appropriate for collection of water samples for volatile analysis. Other bailer types (messenger, bottom fill, etc.) are less desirable, but may be mandated by cost and site conditions.

#### 7.4.1.1 Operation

1. Surround the monitor well with clean plastic sheeting. If using the GPI bailer, insert a vial into the claim and assemble the unit.

2. Attach a line to a clean decontaminated bailer.

3. Lower the bailer slowly and gently into the well, taking care not to shake the casing sides or to splash the bailer into the water. Stop lowering at a point adjacent to the screen.

4. Allow bailer to fill and then slowly and gently retrieve the bailer from the well avoiding contact with the casing, so as not to knock flakes of rust or other foreign materials into the bailer. If using the GPI bailer for collecting volatile organic samples, once at the surface, remove the bailer from the cable. Carefully open the GPI bailer unit and remove the vial. Begin slowly pouring from the bailer, and collect the duplicate samples from the midstream sample.

5. Remove the cap from the sample container and place it on the plastic sheet or in a location where it won't become contaminated. See Section 7.7 for special considerations on VOA samples.

6. Begin slowly pouring from the bailer.

7. Filter and preserve samples as required by sampling plan.

8. Cap the sample container tightly and place prelabeled sample container in a carrier.

9. Replace the well cap.

10. Log all samples in the site logbook and on field data sheets and label all samples.

11. Package samples and complete necessary paperwork.

12. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

### 7.4.2 Submersible Pumps

Although it is recommended that samples not be collected with a submersible pump due to the reasons stated in Section 4.4.2, there are some situations where they may be used.

#### 7.4.2.1 Operation

1. Allow the monitor well to recharge after purging, keeping the pump just above screened section.

2. Attach gate valve to hose (if not already fitted), and reduce flow of water to a manageable sampling rate.

3. Assemble the appropriate bottles.

4. If no gate valve is available, run the water

down the side of a clean jar and fill the sample bottles from the jar.

5. Cap the sample container tightly and place prelabeled sample container in a carrier.

6. Replace the well cap.

7. Log all samples in the site logbook and on the field data sheets and label all samples.

8. Package samples and complete necessary paperwork.

9. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.

10. Upon completion, remove pump and assembly and fully decontaminate prior to setting into the next sample well. Dedicate the tubing to the hole.

### 7.4.3 Non-Contact Gas Bladder Pumps

The use of a non-contact gas positive displacement bladder pump is often mandated by the use of dedicated pumps installed in wells. These pumps are also suitable for shallow (less than 100 feet) wells. They are somewhat difficult to clean, but may be used with dedicated sample tubing to avoid cleaning. These pumps require a power supply and a compressed gas supply (or compressor). They may be operated at variable flow and pressure rates making them ideal for both purging and sampling.

Barcelona (1984) and Nielsen (1985) report that the non-contact gas positive displacement pumps cause the least amount of alteration in sample integrity as compared to other sample retrieval methods.

#### 7.4.3.1. Operation

1. Allow well to recharge after purging.

2. Assemble the appropriate bottles.

3. Turn pump on, increase the cycle time and reduce the pressure to the minimum that will allow the sample to come to the surface.

4. Cap the sample container tightly and place prelabeled sample container in a carrier.

5. Replace the well cap.

6. Log all samples in the site logbook and on field data sheets and label all samples.

7. Package samples and complete necessary paperwork.

8. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

9. On completion, remove the tubing from the well and either replace the Teflon tubing and bladder with new dedicated tubing and bladder or rigorously decontaminate the existing materials.

10. Nonfiltered samples shall be collected directly from the outlet tubing into the sample bottle.

11. For filtered samples, connect the pump outlet tubing directly to the filter unit. The pump pressure should remain decreased so that the pressure build up on the filter does not blow out the pump bladder or displace the filter. For the Geotech barrel filter, no actual connections are necessary so this is not a concern.

### 7.4.4 Suction Pumps

In view of the limitations of these type pumps, they are not recommended for sampling purposes.

### 7.4.5 Inertia Pumps

Inertia pumps may be used to collect samples. It is more common, however, to purge with these pumps and sample with a bailer (Section 7.4.1).

#### 7.4.5.1 Operation

1. Following well evacuation, allow the well to recharge.

2. Assemble the appropriate bottles.

3. Since these pumps are manually operated,

the flow rate may be regulated by the sampler. The sample may be discharged from the pump outlet directly into the appropriate sample container.

4. Cap the sample container tightly and place prelabeled sample container in a carrier.

5. Replace the well cap.

6. Log all samples in the site logbook and on field data sheets and label all samples.

7. Package samples and complete necessary paperwork.

8. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.

9. Upon completion, remove pump and decontaminate or discard, as appropriate.

### 7.4.6. Sample Retrieval - Syringe

A limited number of commercial syringe type samplers are available, (IEA, TIMCO, etc.) some are homemade devices. These devices are claimed to provide good quality samples for volatile analysis, but are severly limited in sample volume and are specific to sampling for volatiles. Essentially, they operated with an evacuated chamber that is lowered down the well, and allowed to fill with the pressure of the water. The entire mechanism is then brought to the surface with the sample. The sample may then be transferred to a sample vial, or the entire unit may be sent as the sample container.

1. Evacuate the syringe if necessary, and lower the sampling device to just below the well screen.

2. Remove the constriction from the device and allow the sample to fill the syringe, apply slight suction as necessary.

3. Bring unit to the surface. If necessary, transfer the sample to vials, as outlined in steps 2 through 7 above.

## 7.5 Filtering

For samples requiring filtering, such as total metals analysis, the filter must be decontaminated prior to and between uses. Filters work by two methods. A barrel filter such as the "Geotech" filter works with a bicycle pump, used to build up positive pressure in the chamber containing the sample which is then forced through the filter paper (minimum size 0.45 μm) into a jar placed underneath. The barrel itself is filled manually from the bailer or directly via the hose of the sampling pump. The pressure must be maintained up to 30 lbs/in$^2$ by periodic pumping.

A vacuum type filter involves two chambers; the upper chamber contains the sample and a filter (minimum size 0.45 μm) divides the chambers. Using a hand pump or a Gilian type pump, air is withdrawn from the lower chamber, creating a vacuum and thus causing the sample to move through the filter into the lower chamber where it is drained into a sample jar. Repeated pumping may be required to drain all the sample into the lower chamber. If preservation of the sample is necessary, this should be done after filtering.

## 7.6 Post Operation

After all samples are collected and preserved, the sampling equipment should be decontaminated prior to sampling another well to prevent cross-contamination of equipment and monitor wells between locations.

1. Decontaminate all equipment.

2. Replace sampling equipment in storage containers.

3. Prepare and transport ground water samples to the laboratory. Check sample documentation and make sure samples are properly packed for shipment.

## 7.7 Special Considerations for VOA Sampling

The proper collection of a sample for volatile organics requires minimal disturbance of the sample to limit volatilization and therefore a loss of volatiles from the sample.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must be to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

The following procedures should be followed:

1. Open the vial, set cap in a clean place, and collect the sample during the middle of the cycle. When collecting duplicates, collect both samples at the same time.

2. Fill the vial to just overflowing. Do not rinse the vial, nor excessively overflow it. There should be a convex meniscus on the top of the vial.

3. Check that the cap has not been contaminated (splashed) and carefully cap the vial. Place the cap directly over the top and screw down firmly. Do not overtighten and break the cap.

4. Invert the vial and tap gently. Observe vial for at least ten (10) seconds. If an air bubble appears, discard the sample and begin again. It is imperative that no entrapped air is in the sample vial.

5. Immediately place the vial in the protective foam sleeve and place into the cooler, oriented so that it is lying on its side, not straight up.

6. The holding time for VOAs is seven days. Samples should be shipped or delivered to the laboratory daily so as not to exceed the holding time. Ensure that the samples remain at 4°C, but do not allow them to freeze.

## 8.0 CALCULATIONS

If it is necessary to calculate the volume of the well, utilize the following equation:

$$\textit{Well volume} = nr^2h\ (cf) \qquad [\textit{Equation } 1]$$

where:

| | | |
|---|---|---|
| $n$ | = | pi |
| $r$ | = | radius of monitoring well (feet) |
| $h$ | = | height of the water column (feet) [This may be determined by subtracting the depth to water from the total depth of the well as measured from the same reference point.] |
| $cf$ | = | conversion factor (gal/ft$^3$) = 7.48 gal/ft$^3$ [In this equation, 7.48 gal/ft$^3$ is the necessary conversion factor.] |

Monitor well diameters are typically 2", 3", 4", or 6". Knowing the diameter of the monitor well, there are a number of standard conversion factors which can be used to simplify the equation above.

The volume, in gallons per linear foot, for various standard monitor well diameters can be calculated as follows:

$$v(gal/ft) = nr^2\ (cf) \qquad [\textit{Equation } 2]$$

where:

| | | |
|---|---|---|
| $n$ | = | pi |
| $r$ | = | radius of monitoring well (feet) |
| $cf$ | = | conversion factor (7.48 gal/ft$^3$) |

For a 2" diameter well, the volume per linear foot can be calculated as follows:

$$\textit{vol/linear ft} = nr^2\ (cf) \qquad [\textit{Equation } 2]$$
$$= 3.14\ (1/12\ ft)^2\ \ 7.48\ gal/ft^3$$
$$= 0.1632\ gal/ft$$

Remember that if you have a 2" diameter well, you must convert this to the radius in feet to be able to use the equation.

The conversion factors for the common size monitor wells are as follows:

| Well diameter | 2" | 3" | 4" | 6" |
|---|---|---|---|---|
| Volume (gal/ft.) | 0.1632 | 0.3672 | 0.6528 | 1.4688 |

If you utilize the conversion factors above, Equation

I should be modified as follows:

$$\textit{Well volume} = (h)(cf) \qquad [\textit{Equation } 3]$$

where:

| | | |
|---|---|---|
| $h$ | = | height of water column (feet) |
| $cf$ | = | the conversion factor calculated from Equation 2 |

The well volume is typically tripled to determine the volume to be purged.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

3. The collection of rinsate blanks is recommended to evaluate potential for cross contamination from the purging and/or sampling equipment.

4. Trip blanks are required if analytical parameters include VOAs.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA or REAC health and safety guidelines. More specifically, depending upon the site specific contaminants, various protective programs must be implemented prior to sampling the first well. The site health and safety plan should be reviewed with specific emphasis placed on the protection program planned for the well sampling tasks. Standard safe operating practices should be followed such as minimizing contact with potential contaminants in both the vapor phase and liquid matrix through the use of respirators and disposable clothing.

When working around volatile organic contaminants:

1. Avoid breathing constituents venting from the well.

2. Pre-survey the well head-space with an FID/PID prior to sampling.

3. If monitoring results indicate organic constituents, sampling activities may be conducted in Level C protection. At a minimum, skin protection will be afforded by disposable protective clothing.

Physical hazards associated with well sampling:

1. Lifting injuries associated with pump and bailers retrieval; moving equipment.

2. Use of pocket knives for cutting discharge hose.

3. Heat/cold stress as a result of exposure to extreme temperatures and protective clothing.

4. Slip, trip, fall conditions as a result of pump discharge.

5. Restricted mobility due to the wearing of protective clothing.

6. Electrical shock associated with use of submersible pumps is possible. Use a GFCI or a copper grounding stake to avoid this problem.

## 12.0 REFERENCES

Barcelona, M.J., Helfrich, J.A., Garske, E.E., and J.P. Gibb, Spring 1984. "A Laboratory Evaluation of Groundwater Sampling Mechanisms," Groundwater

Monitoring Review, 1984 pp. 32-41.

Barcelona, M.J., Helfrich, J.A., and Garske, E.E., "Sampling Tubing Effects on Groundwater Samples", Analy. Chem., Vol. 57, 1985 pp. 460-463.

Driscoll, F.G., Groundwater and Wells (2nd ed.) Johnson Division, UOP Inc., St. Paul, Minnesota, 1986, 1089 pp.

Gibb, J.P., R.M. Schuller, and R.A. Griffin,. Monitoring Well Sampling and Preservation Techniques, EPA-600/9-80-010, 1980. March, 1980.

Instrument Specialties Company, (January). Instruction Manual, Model 2100 Wastewater Sampler, Lincoln, Nebraska, 1980.

Keely, J.F. and Kwasi Boateng, Monitoring Well Installation, Purging and Sampling Techniques - Part I: Conceptualizations, Groundwater V25, No. 3, 1987 pp. 300-313.

Keith, Lawrence H., Principles of Environmental Sampling, American Chemical Society, 1988.

Korte, Nic, and Dennis Ealey,. Procedures for Field Chemical Analyses of Water Samples, U.S. Department of Energy, GJ/TMC-07, Technical Measurements Center, Grand Junction Project Office, 1983.

Korte, Nic, and Peter Kearl,. Procedures for the Collection and Preservation of Groundwater and Surface Water Samples and for the Installation of Monitoring Wells: Second Edition, U.S. Department of Energy, GJ/TMC-08, Technical Measurements Center, Grand Junction Projects Office, 1985.

National Council of the Paper Industry for Air and Stream Improvement, Inc.,. A Guide to Groundwater Sampling, Technical Bulletin No. 362, Madison, New York. January, 1982.

Nielsen, David M. and Yeates, Gillian L., Spring. "A Comparison of Sampling Mechanisms Available for Small-Diameter Groundwater Monitoring Wells," Groundwater Monitoring Review, 1985 pp. 83-99.

Scalf, et al. (M.J. Scalf, McNabb, W. Dunlap, R. Crosby, and J. Fryberger),. Manual for Groundwater Sampling Procedures. R.S. Kerr Environmental Research Laboratory, Office of Research and Development. 1980, Ada, OK.

Sisk, S.W. NEIC Manual for Ground/Surface Investigations at Hazardous Waste Sites, EPA-330/9-81-002, 1981.

U.S. Department of the Interior, National Handbook of Recommended Methods for Water-Data Acquisition, Reston, Virginia.

U.S. Environmental Protection Agency, 1977. Procedures Manual for Groundwater Monitoring at Solid Waste Disposal Facilities. EPA-530/SW-611. August, 1977.

U.S. Code of Federal Regulations, 49 CFR Parts 100 to 177, Transportation revised November 1, 1985.

U.S. Environmental Protection Agency, 1982. Handbook for Chemical and Sample Preservation of Water and Wastewater, EPA-600/4-82-029, Washington, D.C.

U.S. Environmental Protection Agency, 1983. Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020, Washington, D.C.

U.S. Environmental Protection Agency, 1984. Test Methods for Evaluation of Solid Waste, EPA-SW-846, Second Edition, Washington, D.C.

U.S. Environmental Protection Agency, 1981. Manual of Groundwater Quality Sampling Procedures, EPA-600/2-81-160, Washington, D.C.

U.S. Environmental Protection Agency, 1985. Practical Guide for Groundwater Sampling, EPA-600/2-85/104, September, 1985.

U.S. Environmental Protection Agency, 1986. RCRA Groundwater Monitoring Technical Enforcement Guidance Document, OSWER-9950-1, September, 1986.

Weston, 1987. Standard Operations Procedures for Monitor Well Installation. MOUND IGMP/RIP.

U.S. Environmental Protection Agency, 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA-600/4-82-029, Washington, D.C.

--- 1981. Manual of Groundwater Quality

Sampling Procedures, EPA-600/2-81-160, Washington, D.C.

--- 1985. Practice Guide for Groundwater Sampling, EPA-600/2/85-104, September 1985.

Nielsen, David M. and Yeates, Gillian L., Spring 1985. "A Comparison of Sampling Mechanisms Available for Small-Diameter Groundwater Monitoring Wells," Groundwater Monitoring Review, pp. 83-99.

WESTON, 1987. Standard Operating Procedures for Monitor Well Installation. MOUND IGMP/RIP

Barcelona, M.J. Helfrich, J.A., and Garske, E.E., "Sampling Tubing Effects on Groundwater Samples". 1985, Analy. Chem., Vol. 57, pp. 460-463.

# U. S. EPA ENVIRONMENTAL RESPONSE TEAM

## STANDARD OPERATING PROCEDURES



**SOIL SAMPLING**

CONTENTS



SUPERCEDES: SOP #2012; Revision 0.0; 11/16/94; U.S. EPA Contract 68-C4-0022.

1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe the procedures for the collection of representative soil samples. Sampling depths are assumed to be those that can be reached without the use of a drill rig, direct-push, or other mechanized equipment (except for a back-hoe). Analysis of soil samples may determine whether concentrations of specific pollutants exceed established action levels, or if the concentrations of pollutants present a risk to public health, welfare, or the environment.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the actual procedures used should be documented and described in an appropriate site report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Soil samples may be collected using a variety of methods and equipment depending on the depth of the desired sample, the type of sample required (disturbed vs. undisturbed), and the soil type. Near-surface soils may be easily sampled using a spade, trowel, and scoop. Sampling at greater depths may be performed using a hand auger, continuous flight auger, a trier, a split-spoon, or, if required, a backhoe.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Chemical preservation of solids is not generally recommended. Samples should, however, be cooled and protected from sunlight to minimize any potential reaction. The amount of sample to be collected and proper sample container type are discussed in ERT/REAC SOP #2003 Rev. 0.0 08/11/94, *Sample Storage, Preservation and Handling.*

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary potential problems associated with soil sampling - cross contamination of samples and improper sample collection. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Improper sample collection can involve using contaminated equipment, disturbance of the matrix resulting in compaction of the sample, or inadequate homogenization of the samples where required, resulting in variable, non-representative results.

5.0 EQUIPMENT

Soil sampling equipment includes the following:

- Maps/plot plan
- Safety equipment, as specified in the site-specific Health and Safety Plan
- Survey equipment or global positioning system (GPS) to locate sampling points
- Tape measure
- Survey stakes or flags
- Camera and film
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan
- Appropriate size sample containers
- Ziplock plastic bags
- Logbook
- Labels
- Chain of Custody records and custody seals
- Field data sheets and sample labels
- Cooler(s)
- Ice
- Vermiculite
- Decontamination supplies/equipment
- Canvas or plastic sheet
- Spade or shovel
- Spatula
- Scoop
- Plastic or stainless steel spoons
- Trowel(s)
- Continuous flight (screw) auger
- Bucket auger
- Post hole auger
- Extension rods
- T-handle
- Sampling trier
- Thin wall tube sampler
- Split spoons
- Vehimeyer soil sampler outfit
  - Tubes
  - Points
  - Drive head
  - Drop hammer
  - Puller jack and grip
- Backhoe

6.0 REAGENTS

Reagents are not used for the preservation of soil samples. Decontamination solutions are specified in ERT/REAC SOP #2006 Rev. 0.0 08/11/94, *Sampling Equipment Decontamination*, and the site specific work plan.

## 7.0 PROCEDURES

### 7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required.
2. Obtain necessary sampling and monitoring equipment.
3. Decontaminate or pre-clean equipment, and ensure that it is in working order.
4. Prepare schedules and coordinate with staff, client, and regulatory agencies, if appropriate.
5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.
6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors, including extent and nature of contaminant, should be considered when selecting sample location. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. All staked locations should be utility-cleared by the property owner or the On-Scene-Coordinator (OSC) prior to soil sampling; and utility clearance should always be confirmed before beginning work.

### 7.2 Sample Collection

#### 7.2.1 Surface Soil Samples

Collection of samples from near-surface soil can be accomplished with tools such as spades, shovels, trowels, and scoops. Surface material is removed to the required depth and a stainless steel or plastic scoop is then used to collect the sample.

This method can be used in most soil types but is limited to sampling at or near the ground surface. Accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by the sample team member. A flat, pointed mason trowel to cut a block of the desired soil is helpful when undisturbed profiles are required. Tools plated with chrome or other materials should not be used. Plating is particularly common with garden implements such as potting trowels.

The following procedure is used to collect surface soil samples:

1. Carefully remove the top layer of soil or debris to the desired sample depth with a pre-cleaned spade.

2. Using a pre-cleaned, stainless steel scoop, plastic spoon, or trowel, remove and discard a thin layer of soil from the area which came in contact with the spade.

3. If volatile organic analysis is to be performed, transfer the sample directly into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.2 Sampling at Depth with Augers and Thin Wall Tube Samplers

This system consists of an auger, or a thin-wall tube sampler, a series of extensions, and a "T" handle (Figure 1, Appendix A). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the auger. If a core sample is to be collected, the auger tip is then replaced with a thin wall tube sampler. The system is then lowered down the borehole, and driven into the soil to the completion depth. The system is withdrawn and the core is collected from the thin wall tube sampler.

Several types of augers are available; these include: bucket type, continuous flight (screw), and post-hole augers. Bucket type augers are better for direct sample recovery because they provide a large volume of sample in a short time. When continuous flight augers are used, the sample can be collected directly from the flights. The continuous flight augers are satisfactory when a composite of the complete soil column is desired. Post-hole augers have limited utility for sample collection as they are designed to cut through fibrous, rooted, swampy soil and cannot be used below a depth of approximately three feet.

The following procedure is used for collecting soil samples with the auger:

1. Attach the auger bit to a drill rod extension, and attach the "T" handle to the drill rod.

2. Clear the area to be sampled of any surface debris (e.g., twigs, rocks, litter). It may be advisable to remove the first three to six inches of surface soil for an area approximately six inches in radius around the drilling location.

3. Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents accidental brushing of loose material back down the borehole when removing the auger or adding drill rods. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.

4. After reaching the desired depth, slowly and carefully remove the auger from the hole. When sampling directly from the auger, collect the sample after the auger is removed from the hole and proceed to Step 10.

5. Remove auger tip from the extension rods and replace with a pre-cleaned thin wall tube sampler. Install the proper cutting tip.

6. Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the soil. Do not scrape the borehole sides. Avoid hammering the rods as the vibrations may cause the boring walls to collapse.

7. Remove the tube sampler, and unscrew the drill rods.

8. Remove the cutting tip and the core from the device.

9. Discard the top of the core (approximately 1 inch), as this possibly represents material collected before penetration of the layer of concern. Place the remaining core into the appropriate labeled sample container. Sample homogenization is not required.

10. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly.

    When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the auger bit to the drill and assembly, and follow steps 3 through 11, making sure to decontaminate the auger and tube sampler between samples.

12. Abandon the hole according to applicable state regulations. Generally, shallow holes can simply be backfilled with the removed soil material.

7.2.3 Sampling with a Trier

The system consists of a trier, and a "T" handle. The auger is driven into the soil to be sampled and used to extract a core sample from the appropriate depth.

The following procedure is used to collect soil samples with a sampling trier:

1. Insert the trier (Figure 2, Appendix A) into the material to be sampled at a 0° to 45° angle from horizontal. This orientation minimizes the spillage of sample.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.4 Sampling at Depth with a Split Spoon (Barrel) Sampler

Split spoon sampling is generally used to collect undisturbed soil cores of 18 or 24 inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling. The split spoon is then driven to its sampling depth through the bottom of the augured hole and the core extracted.

When split spoon sampling is performed to gain geologic information, all work should

be performed in accordance with ASTM D1586-98, "Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils".

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe on the bottom and the head piece on top.

2. Place the sampler in a perpendicular position on the sample material.

3. Using a well ring, drive the tube. Do not drive past the bottom of the head piece or compression of the sample will result.

4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth.

5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally. This sampler is typically available in 2 and 3 1/2 inch diameters. A larger barrel may be necessary to obtain the required sample volume.

6. Without disturbing the core, transfer it to appropriate labeled sample container(s) and seal tightly.

7.2.5 Test Pit/Trench Excavation

A backhoe can be used to remove sections of soil, when detailed examination of soil characteristics are required. This is probably the most expensive sampling method because of the relatively high cost of backhoe operation.

The following procedures are used for collecting soil samples from test pits or trenches:

1. Prior to any excavation with a backhoe, it is important to ensure that all sampling locations are clear of overhead and buried utilities.

2. Review the site specific Health & Safety plan and ensure that all safety precautions including appropriate monitoring equipment are installed as required.

3. Using the backhoe, excavate a trench approximately three feet wide and approximately one foot deep below the cleared sampling location. Place excavated soils on plastic sheets. Trenches greater than five feet deep must be sloped or protected by a shoring system, as required by OSHA regulations.

4. A shovel is used to remove a one to two inch layer of soil from the vertical face of the pit where sampling is to be done.

5. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In many instances, samples can be collected directly from the backhoe bucket.

6. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7. Abandon the pit or excavation according to applicable state regulations. Generally, shallow excavations can simply be backfilled with the removed soil material.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITY ASSURANCE/QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration

activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OHSA and corporate health and safety procedures, in addition to the procedures specified in the site specific Health & Safety Plan..

12.0 REFERENCES

Mason, B.J. 1983. Preparation of Soil Sampling Protocol: Technique and Strategies. EPA-600/4-83-020.

Barth, D.S. and B.J. Mason. 1984. Soil Sampling Quality Assurance User's Guide. EPA-600/4-84-043.

U.S. Environmental Protection Agency. 1984 Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA-600/4-84-076.

de Vera, E.R., B.P. Simmons, R.D. Stephen, and D.L. Storm. 1980. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018.

ASTM D 1586-98, ASTM Committee on Standards, Philadelphia, PA.

APPENDIX A
Figures
SOP #2012
February 2000

FIGURE 1. Sampling Augers

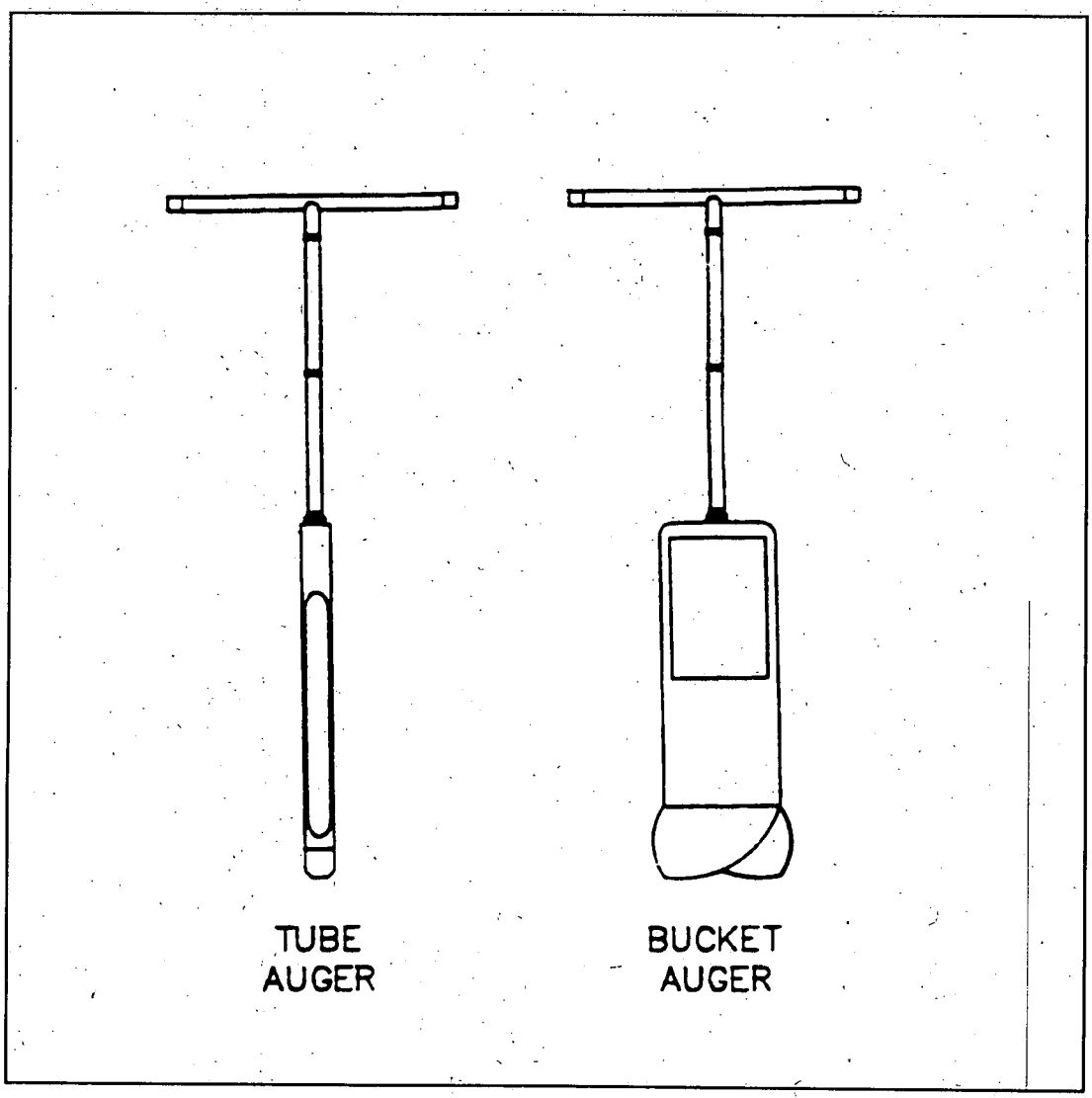
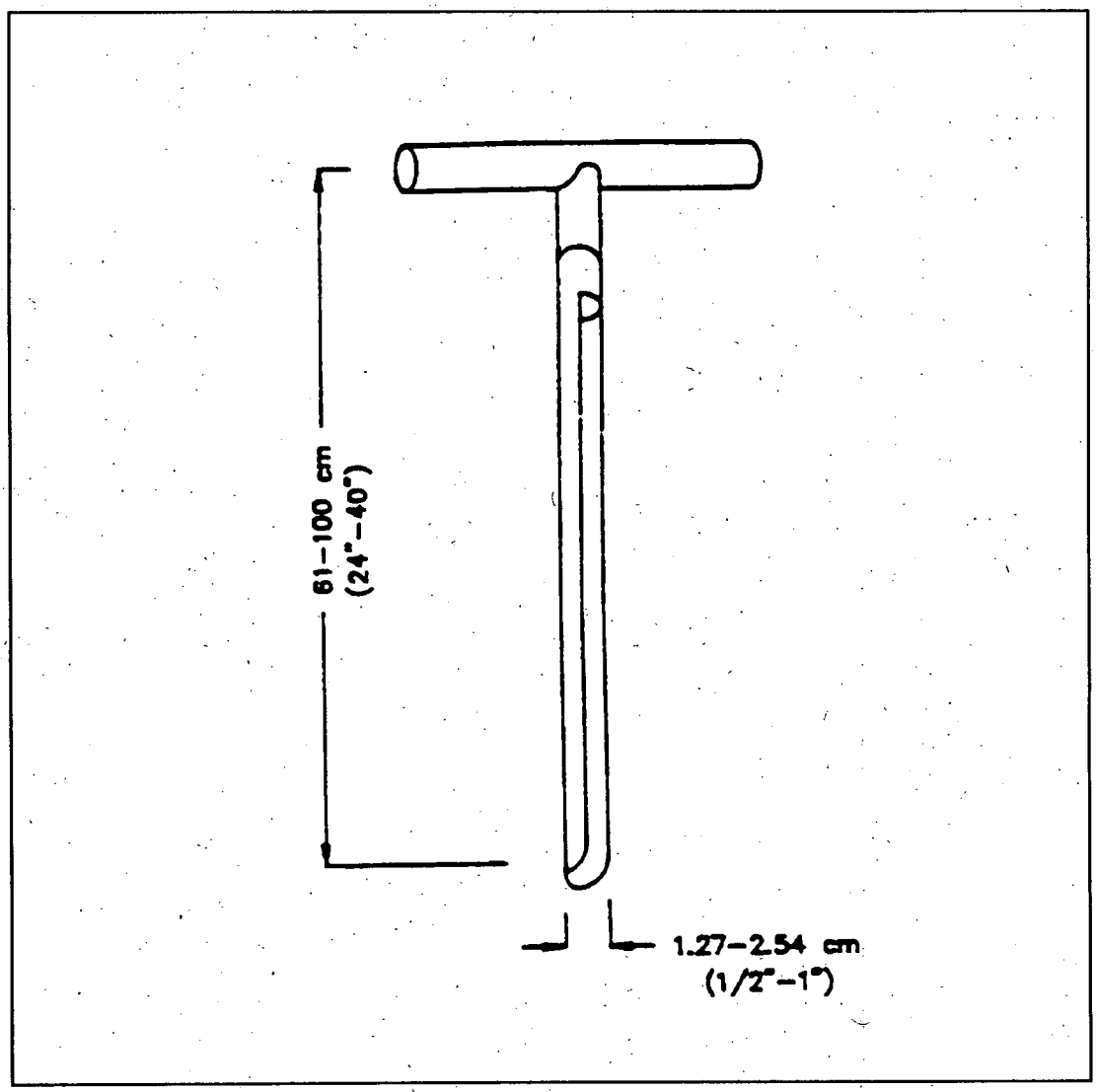


FIGURE 2. Sampling Trier



# SURFACE WATER SAMPLING

SOP#: 2013
DATE: 11/17/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the collection of representative liquid samples, both aqueous and non-aqueous from streams, rivers, lakes, ponds, lagoons, and surface impoundments. It includes samples collected from depth, as well as samples collected from the surface.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Sampling situations vary widely, therefore, no universal sampling procedure can be recommended. However, sampling of both aqueous and non-aqueous liquids from the above mentioned sources is generally accomplished through the use of one of the following samplers or techniques:

- Kemmerer bottle
- Bacon bomb sampler
- Dip sampler
- Direct method

These sampling techniques will allow for the collection of representative samples from the majority of surface waters and impoundments encountered.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Once samples have been collected, the following procedure should be followed:

1. Transfer the sample(s) into suitable, labeled sample containers.
2. Preserve the sample if appropriate, or use pre-preserved sample bottles. Do not overfill bottles if they are pre-preserved.
3. Cap the container, place in a ziploc plastic bag and cool to 4°C.
4. Record all pertinent data in the site logbook and on field data sheets.
5. Complete the Chain of Custody record.
6. Attach custody seals to cooler prior to shipment.
7. Decontaminate all sampling equipment prior to the collection of additional samples with that sampling device.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary interferences or potential problems with surface water sampling. These include cross contamination of samples and improper sample collection.

1. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Refer to the Sampling Equipment Decontamination SOP.

2. Improper sample collection can involve using contaminated equipment, disturbance of the stream or impoundment substrate, and sampling in an obviously disturbed area.

Following proper decontamination procedures and minimizing disturbance of the sample site will eliminate these problems.

## 5.0 EQUIPMENT/APPARATUS

Equipment needed for collection of surface water samples may include (depending on technique chosen):

- Kemmerer bottles
- Bacon bomb sampler
- Dip sampler
- Line and messengers
- Sample bottles/preservatives
- Ziploc bags
- Ice
- Coolers
- Chain of Custody records, custody seals
- Field data sheets
- Decontamination equipment
- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Logbook/waterproof pen
- Sample bottle labels

## 6.0 REAGENTS

Reagents will be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed.

## 7.0 PROCEDURES

### 7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.

2. Obtain the necessary sampling and monitoring equipment.

3. Decontaminate or pre-clean equipment, and ensure that it is in working order.

4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry, in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. If required the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If collecting sediment samples, this procedure may disturb the bottom.

### 7.2 Representative Sampling Considerations

In order to collect a representative sample, the hydrology and morphometrics of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons, or impoundments, flow patterns in streams, and appropriate sample locations and depths.

Water quality data should be collected in impoundments, and to determine if stratification is present. Measurements of dissolved oxygen, pH, and temperature can indicate if strata exist which would effect analytical results. Measurements should be collected at one-meter intervals from the substrate to the surface using the appropriate instrument (i.e., a Hydrolab or equivalent).

Water quality measurements such as dissolved oxygen, pH, temperature, conductivity, and oxidation-reduction potential can assist in the interpretation of analytical data and the selection of sampling sites and depths when surface water samples are collected.

Generally, the deciding factors in the selection of a sampling device for sampling liquids in streams, rivers, lakes, ponds, lagoons, and surface impoundments are:

1. Will the sample be collected from shore or from a boat?

2. What is the desired depth at which you wish to collect the sample?

3. What is the overall depth and flow direction of river or stream?

4. What type of sample will be collected (i.e., water or lagoon liquids)?

### 7.2.1 Sampler Composition

The appropriate sampling device must be of a proper composition. Selection of samplers constructed of glass, stainless steel, PVC or PFTE (Teflon) should be based upon the analyses to be performed.

## 7.3 Sample Collection

### 7.3.1 Kemmerer Bottle

A Kemmerer bottle (Figure 1, Appendix A) may be used in most situations where site access is from a boat or structure such as a bridge or pier, and where samples at depth are required. Sampling procedures are as follows:

1. Use a properly decontaminated Kemmerer bottle. Set the sampling device so that the sampling end pieces (upper and lower stoppers) are pulled away from the sampling tube (body), allowing the substance to be sampled to pass through this tube.

2. Lower the pre-set sampling device to the predetermined depth. Avoid bottom disturbance.

3. When the Kemmerer bottle is at the required depth, send down the messenger, closing the sampling device.

4. Retrieve the sampler and discharge from the bottom drain the first 10-20 mL to clear any potential contamination of the valve. Transfer the sample to the appropriate sample container.

### 7.3.2 Bacon Bomb Sampler

A bacon bomb sampler (Figure 2, Appendix A) may be used in situations similar to those outlined for the Kemmerer bottle. Sampling procedures are as follows:

1. Lower the bacon bomb sampler carefully to the desired depth, allowing the line for the trigger to remain slack at all times. When the desired depth is reached, pull the trigger line until taut. This will allow the sampler to fill.

2. Release the trigger line and retrieve the sampler.

3. Transfer the sample to the appropriate sample container by pulling up on the trigger.

### 7.3.3 Dip Sampler

A dip sampler (Figure 3, Appendix A) is useful in situations where a sample is to be recovered from an outfall pipe or along a lagoon bank where direct access is limited. The long handle on such a device allows access from a discrete location. Sampling procedures are as follows:

1. Assemble the device in accordance with the manufacturer's instructions.

2. Extend the device to the sample location and collect the sample by dipping the sampler into the substance.

3. Retrieve the sampler and transfer the sample to the appropriate sample container.

### 7.3.4 Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect water samples from the surface directly into the sample bottle. This method is not to be used for sampling lagoons or other impoundments where contact with contaminants is a concern.

Using adequate protective clothing, access the sampling station by appropriate means. For shallow stream stations, collect the sample under the water surface while pointing the sample container upstream; the container must be upstream of the collector. Avoid disturbing the substrate. For lakes and other impoundments, collect the sample under the water surface avoiding surface debris and the boat wake.

When using the direct method, do not use pre-preserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA and corporate health and safety procedures.

More specifically, when sampling lagoons or surface impoundments containing known or suspected hazardous substances, adequate precautions must be taken to ensure the safety of sampling personnel. The sampling team member collecting the sample should not get too close to the edge of the impoundment, where bank failure may cause him/her to lose his/her balance. The person performing the sampling should be on a lifeline and be wearing adequate protective equipment. When conducting sampling from a boat in an impoundment or flowing waters, appropriate boating safety procedures should be followed.

## 12.0 REFERENCES

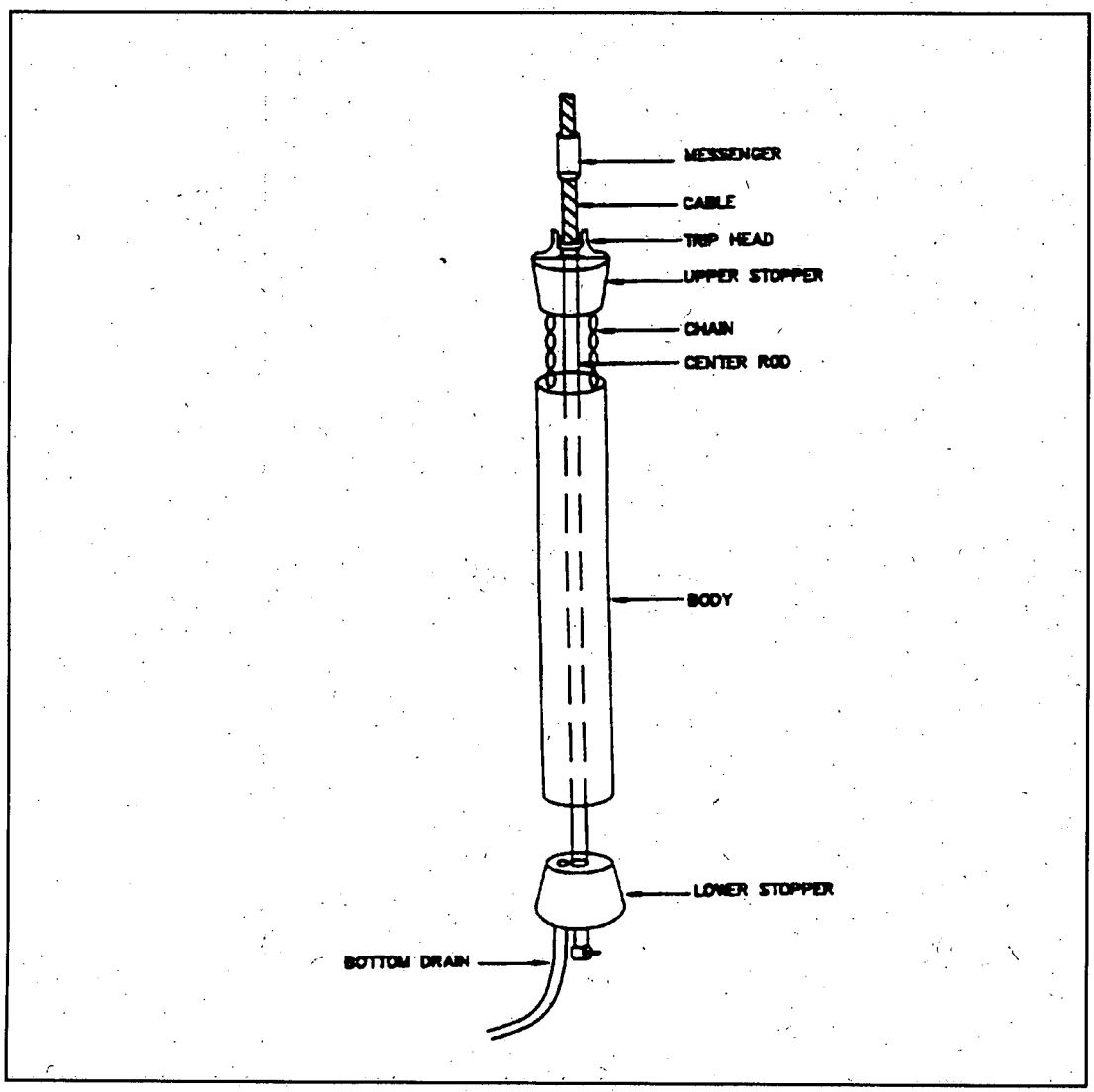
U.S. Geological Survey. 1977. National Handbook or Recommended Methods for Water Data Acquisition. Office of Water Data Coordination Reston, Virginia. (Chapter Updates available).

U.S. Environmental Protection Agency. 1984. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA/600/4-84-076.

# APPENDIX A

Figures

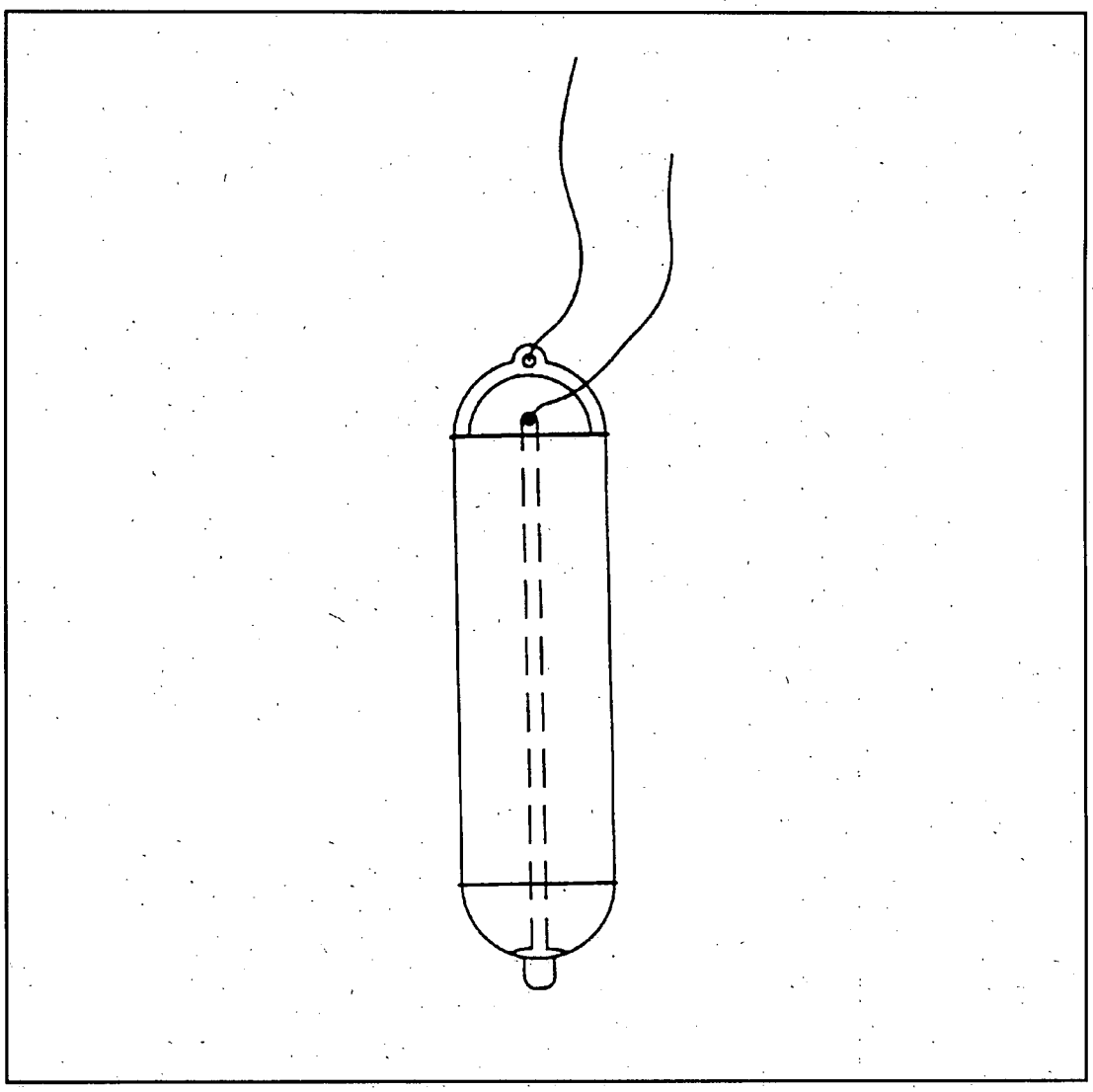
FIGURE 1. Kemmerer Bottle



## APPENDIX A (Cont'd)

Figures

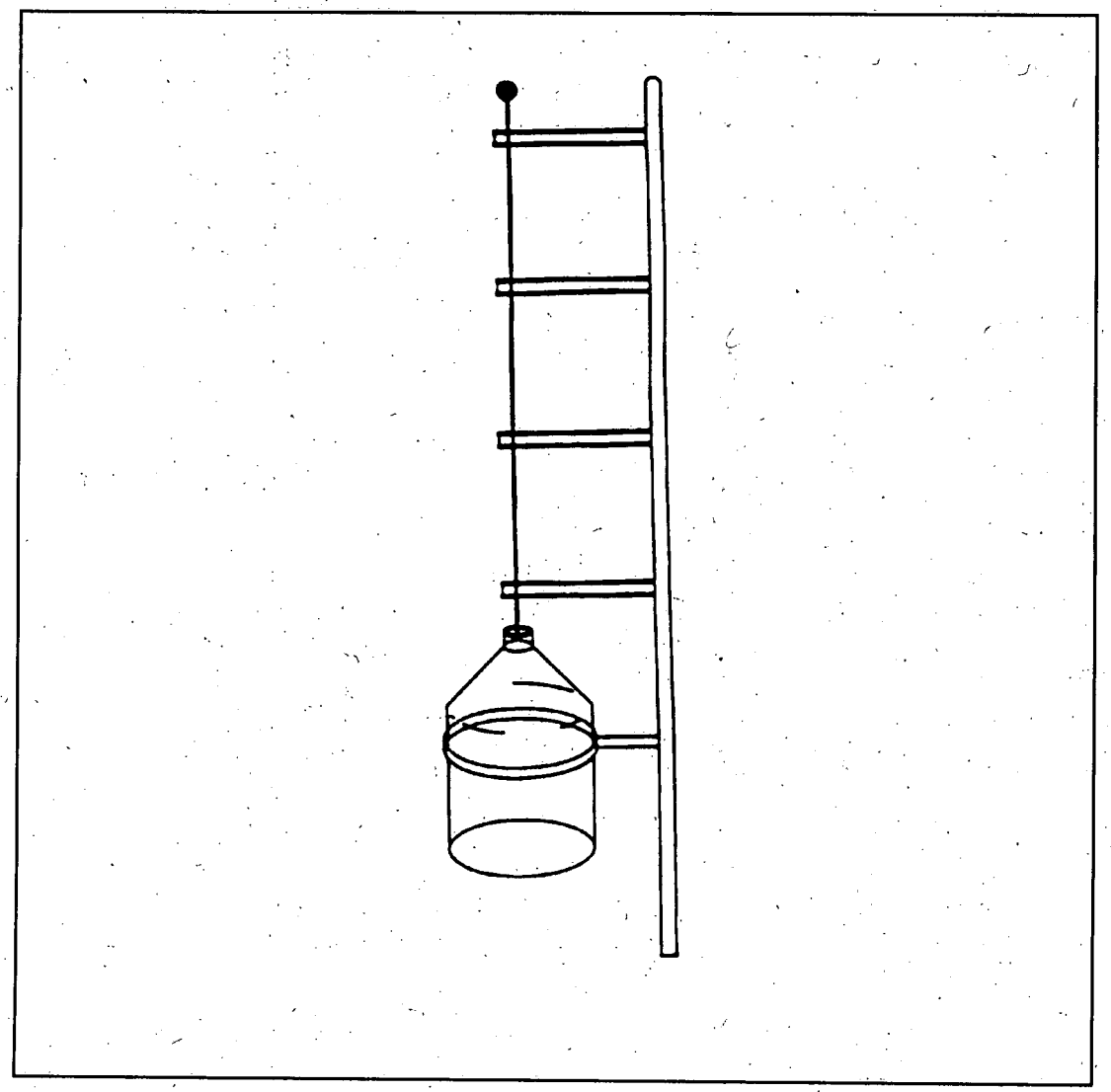
FIGURE 2. Bacon Bomb Sampler



## APPENDIX A (Cont'd)

Figures

FIGURE 3. Dip Sampler



# SEDIMENT SAMPLING

SOP#: 2016
DATE: 11/17/94
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the collection of representative sediment samples. Analysis of sediment may be biological, chemical, or physical in nature and may be used to determine the following:

- toxicity;
- biological availability and effects of contaminants;
- benthic biota;
- extent and magnitude of contamination;
- contaminant migration pathways and source;
- fate of contaminants;
- grain size distribution.

The methodologies discussed in this SOP are applicable to the sampling of sediment in both flowing and standing water. They are generic in nature and may be modified in whole or part to meet the handling and analytical requirements of the contaminants of concern, as well as the constraints presented by site conditions and equipment limitations. However, if modifications occur, they should be documented in a site or personal logbook and discussed in reports summarizing field activities and analytical results.

For the purposes of this procedure, sediments are those mineral and organic materials situated beneath an aqueous layer. The aqueous layer may be either static, as in lakes, ponds, and impoundments; or flowing, as in rivers and streams.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Sediment samples may be collected using a variety of methods and equipment, depending on the depth of the aqueous layer, the portion of the sediment profile required (surface vs. subsurface), the type of sample required (disturbed vs. undisturbed), contaminants present, and sediment type.

Sediment is collected from beneath an aqueous layer either directly, using a hand held device such as a shovel, trowel, or auger; or indirectly, using a remotely activated device such as an Ekman or Ponar dredge. Following collection, sediment is transferred from the sampling device to a sample container of appropriate size and construction for the analyses requested. If composite sampling techniques are employed, multiple grabs are placed into a container constructed of inert material, homogenized, and transferred to sample containers appropriate for the analyses requested. The homogenization procedure should not be used if sample analysis includes volatile organics; in this case, sediment, or multiple grabs of sediment, should be transferred directly from the sample collection device or homogenization container to the sample container.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

1. Chemical preservation of solids is generally not recommended. Cooling to 4°C is usually the best approach, supplemented by the appropriate holding time for the analyses requested.

2. Wide mouth glass containers with Teflon lined caps are utilized for sediment samples. The sample volume is a function of the analytical requirements and will be specified in the Work Plan.

3. If analysis of sediment from a discrete depth or location is desired, sediment is transferred directly from the sampling device to a labeled sample container(s) of appropriate size and construction for the analyses

requested. Transfer is accomplished with a stainless steel or plastic lab spoon or equivalent.

4. If composite sampling techniques or multiple grabs are employed, equal portions of sediment from each location are deposited into a stainless steel, plastic, or other appropriate composition (e.g., Teflon) containers. The sediment is homogenized thoroughly to obtain a composite representative of the area sampled. The composite sediment sample is transferred to a labeled container(s) of appropriate size and construction for the analyses requested. Transfer of sediment is accomplished with a stainless steel or plastic lab spoon or equivalent. Samples for volatile organic analysis must be transferred directly from the sample collection device or pooled from multiple areas in the homogenization container prior to mixing. This is done to minimize loss of contaminant due to volatilization during homogenization.

5. All sampling devices should be decontaminated, then wrapped in aluminum foil. The sampling device should remain in this wrapping until it is needed. Each sampling device should be used for only one sample. Disposable sampling devices for sediment are generally impractical due to cost and the large number of sediment samples which may be required. Sampling devices should be cleaned in the field using the decontamination procedure described in the Sampling Equipment Decontamination SOP.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Substrate particle size and organic matter content are a direct consequence of the flow characteristics of a waterbody. Contaminants are more likely to be concentrated in sediments typified by fine particle size and a high organic matter content. This type of sediment is most likely to be collected from depositional zones. In contrast, coarse sediments with low organic matter content do not typically concentrate pollutants and are generally found in erosional zones. The selection of a sampling location can, therefore, greatly influence the analytical results and should be justified and specified in the Work Plan.

## 5.0 EQUIPMENT/APPARATUS

Equipment needed for collection of sediment samples may include:

- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Stainless steel, plastic, or other appropriate composition bucket
- 4-oz., 8-oz., and one-quart wide mouth jars w/Teflon lined lids
- Ziploc plastic bags
- Logbook
- Sample jar labels
- Chain of Custody records, field data sheets
- Cooler(s)
- Ice
- Decontamination supplies/equipment
- Spade or shovel
- Spatula
- Scoop
- Trowel
- Bucket auger
- Tube auger
- Extension rods
- "T" handle
- Sediment coring device (tube, drive head, eggshell check value, nosecone, acetate tube, extension rods, "T" handle)
- Ponar dredge
- Ekman dredge
- Nylon rope or steel cable
- Messenger device

## 6.0 REAGENTS

Reagents are not used for preservation of sediment samples. Decontamination solutions are specified in the Sampling Equipment Decontamination SOP.

## 7.0 PROCEDURES

### 7.1 Preparation

1. Determine the objective(s) and extent of the sampling effort. The sampling methods to be employed, and the types and amounts of equipment and supplies required will be a function of site characteristics and objectives of the study.

2. Obtain the necessary sampling and monitoring equipment.

3. Prepare schedules, and coordinate with staff, client, and regulatory agencies, if appropriate.

4. Decontaminate or preclean equipment, and ensure that it is in working order.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors including flow regime, basin morphometry, sediment characteristics, depth of overlying aqueous layer, contaminant source, and extent and nature of contamination should be considered when selecting sample locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

### 7.2 Sample Collection

Selection of a sampling device is most often contingent upon: (1) the depth of water at the sampling location, and (2) the physical characteristics of the sediment to be sampled. The following procedures may be utilized:

#### 7.2.1 Sampling Surface Sediment with a Trowel or Scoop from Beneath a Shallow Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth and a shallow aqueous layer is considered to range from 0 to 12 inches in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with tools such as spades, shovels, trowels, and scoops. Although this method can be used to collect both unconsolidated/consolidated sediment, it is limited somewhat by the depth and movement of the aqueous layer. Deep and rapidly flowing water render this method less accurate than others discussed below. However, representative samples can be collected with this procedure in shallow sluggish water provided care is demonstrated by the sample team member. A stainless steel or plastic sampling implement will suffice in most applications. Care should be exercised to avoid the use of devices plated with chrome or other materials; plating is particularly common with garden trowels.

The following procedure will be used to collect sediment with a scoop, shovel, or trowel:

1. Using a decontaminated sampling implement, remove the desired thickness and volume of sediment from the sampling area.

2. Transfer the sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

3. Surface water should be decanted from the sample or homogenization container prior to sealing or transfer; care should be taken to retain the fine sediment fraction during this procedure.

#### 7.2.2 Sampling Surface Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of bucket auger or tube auger, a series of extensions, and a "T" handle (Figure 1, Appendix A). The use of additional extensions in conjunction with a bucket auger can increase the depth of water from which sediment can be collected from 24 inches to 10 feet or more. However, sample handling and manipulation increases

in difficulty with increasing depth of water. The bucket auger or tube auger is driven into the sediment and used to extract a core. The various depths represented by the core are homogenized or a subsample of the core is taken from the appropriate depth.

The following procedure will be used to collect sediment samples with a bucket auger or tube auger:

1. An acetate core may be inserted into the bucket auger or tube auger prior to sampling if characteristics of the sediments or waterbody warrant. By using this technique, an intact core can be extracted.

2. Attach the auger head to the required length of extensions, then attach the "T" handle to the upper extension.

3. Clear the area to be sampled of any surface debris.

4. Insert the bucket auger or tube auger into the sediment at a 0° to 20° angle from vertical. This orientation minimizes spillage of the sample from the sampler upon extraction from the sediment and water.

5. Rotate the auger to cut a core of sediment.

6. Slowly withdraw the auger; if using a tube auger, make sure that the slot is facing upward.

7. Transfer the sample or a specified aliquot of sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

### 7.2.3 Sampling Deep Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer

For the purpose of this method, deep sediment is considered to range from six to greater than 18 inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches. Collection of deep sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a bucket auger, a tube auger, a series of extensions and a "T" handle. The use of additional extensions can increase the depth of water from which sediment can be collected from 24 inches to five feet or more. However, water clarity must be high enough to permit the sampler to directly observe the sampling operation. In addition, sample handling and manipulation increases in difficulty with increasing depth of water. The bucket auger is used to bore a hole to the upper range of the desired sampling depth and then withdrawn. The tube auger is then lowered down the borehole, and driven into the sediment to the lower range of the desired sampling depth. The tube is then withdrawn and the sample recovered from the tube. This method can be used to collect firmly consolidated sediments, but is somewhat limited by the depth of the aqueous layer, and the integrity of the initial borehole.

The following procedure will be used to collect deep sediment samples with a bucket auger and a tube auger:

1. Attach the bucket auger bit to the required lengths of extensions, then attach the "T" handle to the upper extension.

2. Clear the area to be sampled of any surface debris.

3. Begin augering, periodically removing any accumulated sediment (i.e., cuttings) from the auger bucket. Cuttings should be disposed of far enough from the sampling area to minimize cross contamination of various depths.

4. After reaching the upper range of the desired depth, slowly and carefully remove bucket auger from the boring.

5. Attach the tube auger bit to the required lengths of extensions, then attach the "T" handle to the upper extension.

6. Carefully lower tube auger down borehole using care to avoid making contact with the borehole sides and, thus, cross contaminating the sample. Gradually force tube auger into sediment to the lower range of the desired sampling depth. Hammering of the tube auger to facilitate coring should be avoided as the vibrations may cause the boring walls

to collapse.

7. Remove tube auger from the borehole, again taking care to avoid making contact with the borehole sides and, thus, cross contaminating the sample.

8. Discard the top of core (approximately 1 inch); as this represents material collected by the tube auger before penetration to the layer of concern.

9. Transfer sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

### 7.2.4 Sampling Surface Sediment with an Ekman or Ponar Dredge from Beneath a Shallow or Deep Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth. Collection of surface sediment can be accomplished with a system consisting of a remotely activated device (dredge) and a deployment system. This technique consists of lowering a sampling device (dredge) to the surface of the sediment by use of a rope, cable, or extended handle. The mechanism is activated, and the device entraps sediment in spring loaded or lever operated jaws.

An Ekman dredge is a lightweight sediment sampling device with spring activated jaws. It is used to collect moderately consolidated, fine textured sediment. The following procedure will be used for collecting sediment with an Ekman dredge (Figure 2, Appendix A):

1. Attach a sturdy nylon rope or stainless steel cable through the hole on the top of the bracket, or secure the extension handle to the bracket with machine bolts.

2. Attach springs to both sides of the jaws. Fix the jaws so that they are in open position by placing trip cables over the release studs. Ensure that the hinged doors on the dredge top are free to open.

3. Lower the sampler to a point 4 to 6 inches above the sediment surface.

4. Drop the sampler to the sediment.

5. Trigger the jaw release mechanism by lowering a messenger down the line, or by depressing the button on the upper end of the extension handle.

6. Raise the sampler and slowly decant any free liquid through the top of the sampler. Care should be taken to retain the fine sediment fraction during this procedure.

7. Open the dredge jaws and transfer the sample into a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment grabs until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

A Ponar dredge is a heavyweight sediment sampling device with weighted jaws that are lever or spring activated. It is used to collect consolidated fine to coarse textured sediment. The following procedure will be used for collecting sediment with a Ponar dredge (Figure 3, Appendix A):

1. Attach a sturdy nylon rope or steel cable to the ring provided on top of the dredge.

2. Arrange the Ponar dredge with the jaws in the open position, setting the trip bar so the sampler remains open when lifted from the top. If the dredge is so equipped, place the spring loaded pin into the aligned holes in the trip bar.

3. Slowly lower the sampler to a point approximately two inches above the sediment.

4. Drop the sampler to the sediment. Slack on

the line will release the trip bar or spring loaded pin; pull up sharply on the line closing the dredge.

5. Raise the dredge to the surface and slowly decant any free liquid through the screens on top of the dredge. Care should be taken to retain the fine sediment fraction during this operation.

6. Open the dredge and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenized and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

### 7.2.5 Sampling Subsurface Sediment with a Coring Device from Beneath a Shallow Aqueous Layer

For purposes of this method, subsurface sediment is considered to range from 6 to 24 inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches in depth. Collection of subsurface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a tube sampler, acetate tube, eggshell check valve, nosecone, extensions, and "T" handle, or drivehead. The use of additional extensions can increase the depth of water from which sediment can be collected from 24 inches to 10 feet or more. This sampler may be used with either a drive hammer for firm sediment, or a "T" handle for soft sediment. However, sample handling and manipulation increases in difficulty with increasing depth of water.

The following procedure describes the use of a sample coring device (Figure 4, Appendix A) used to collect subsurface sediments.

1. Assemble the coring device by inserting the acetate core into the sampling tube.

2. Insert the "egg shell" check valve into the lower end of the sampling tube with the convex surface positioned inside the acetate core.

3. Screw the nosecone onto the lower end of the sampling tube, securing the acetate tube and eggshell check valve.

4. Screw the handle onto the upper end of the sampling tube and add extension rods as needed.

5. Place the sampler in a perpendicular position on the sediment to be sampled.

6. If the "T" handle is used, place downward pressure on the device until the desired depth is reached. After the desired depth is reached, rotate the sampler to shear off the core at the bottom. Slowly withdraw the sampler from the sediment and proceed to Step 15.

7. If the drive hammer is selected, insert the tapered handle (drive head) of the drive hammer through the drive head.

8. Drive the sampler into the sediment to the desired depth.

9. Record the length of the tube that penetrated the sample material, and the number of blows required to obtain this depth.

10. Remove the drive hammer and fit the keyhole-like opening on the flat side of the hammer onto the drive head. In this position, the hammer serves as a handle for the sampler.

11. Rotate the sampler to shear off the core at the bottom.

12. Lower the sampler handle (hammer) until it just clears the two ear-like protrusions on the drive head, and rotate about 90°.

13. Slowly withdraw the sampler from the sediment. If the drivehead was used, pull the hammer upwards and dislodge the sampler from the sediment.

14. Carefully remove the coring device from the water.

15. Unscrew the nosecone and remove the eggshell check valve.

16. Slide the acetate core out of the sampler tube. Decant surface water, using care to retain the fine sediment fraction. If head space is present in the upper end, a hacksaw may be used to shear the acetate tube off at the sediment surface. The acetate core may then be capped at both ends. Indicate on the acetate tube the appropriate orientation of the sediment core using a waterproof marker. The sample may be used in this fashion, or the contents transferred to a sample or homogenization container.

17. Open the acetate tube and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

## 8.0 CALCULATIONS

This section is not applicable to this SOP.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA/OSHA and Corporate health and safety procedures.

More specifically, when sampling sediment from waterbodies, physical hazards must be identified and adequate precautions must be taken to ensure the safety of the sampling team. The team member collecting the sample should not get too close to the edge of the waterbody, where bank failure may cause loss of balance. To prevent this, the person performing the sampling should be on a lifeline, and be wearing adequate protective equipment. If sampling from a vessel is determined to be necessary, appropriate protective measures must be implemented.

## 12.0 REFERENCES

Mason, B.J., Preparation of Soil Sampling Protocol: Technique and Strategies. 1983 EPA-600/4-83-020.

Barth, D.S. and B.J. Mason, Soil Sampling Quality Assurance User's Guide. 1984 EPA-600/4-84-043.

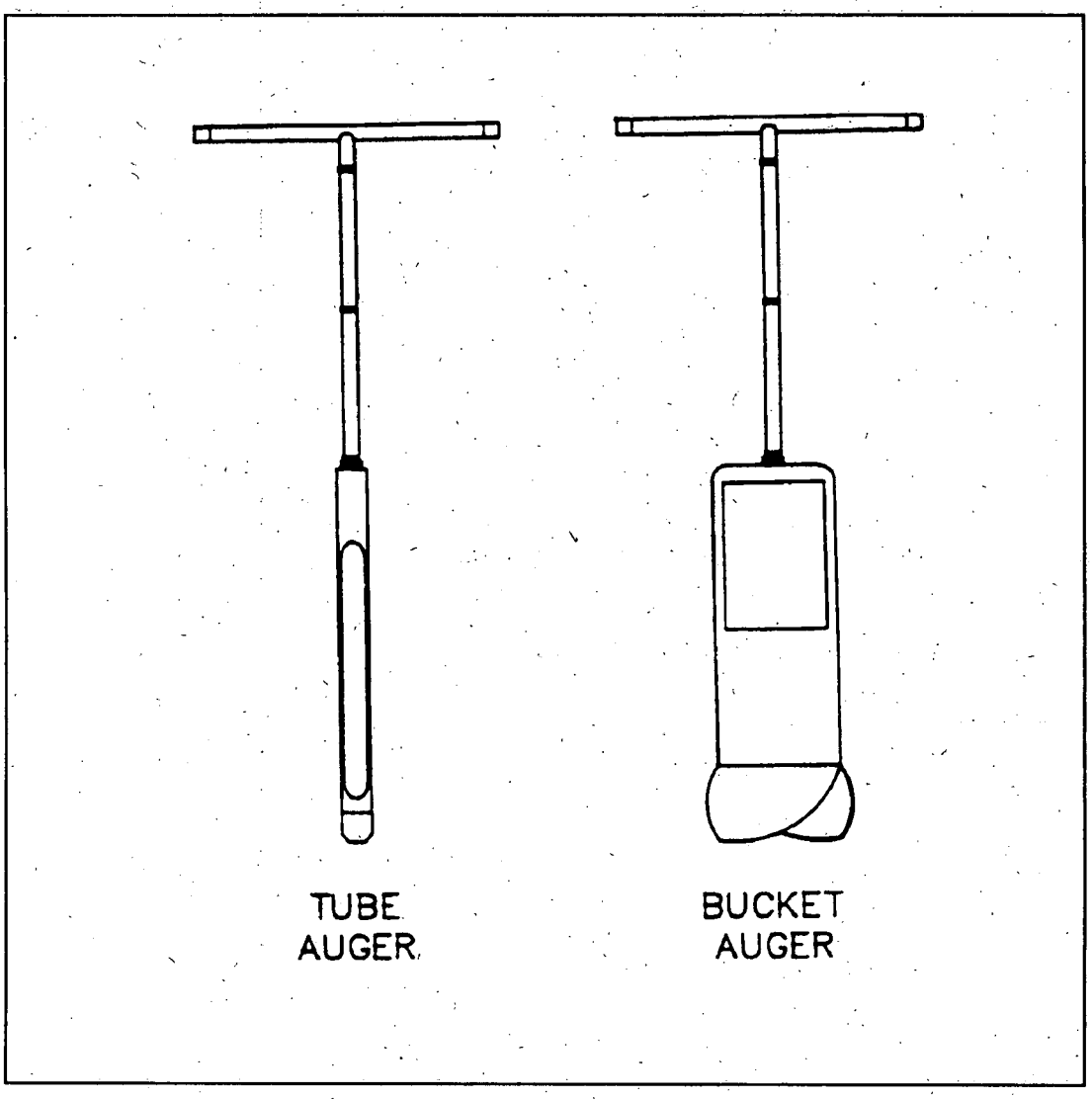
U.S. EPA. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. 1984 EPA-600/4-84-076.

de Vera, E.R., B.P. Simmons, R.D. Stephen, and D.L. Storm. Samplers and Sampling Procedures for Hazardous Waste Streams. 1980 EPA-600/2-80-018.

# APPENDIX A

Figures

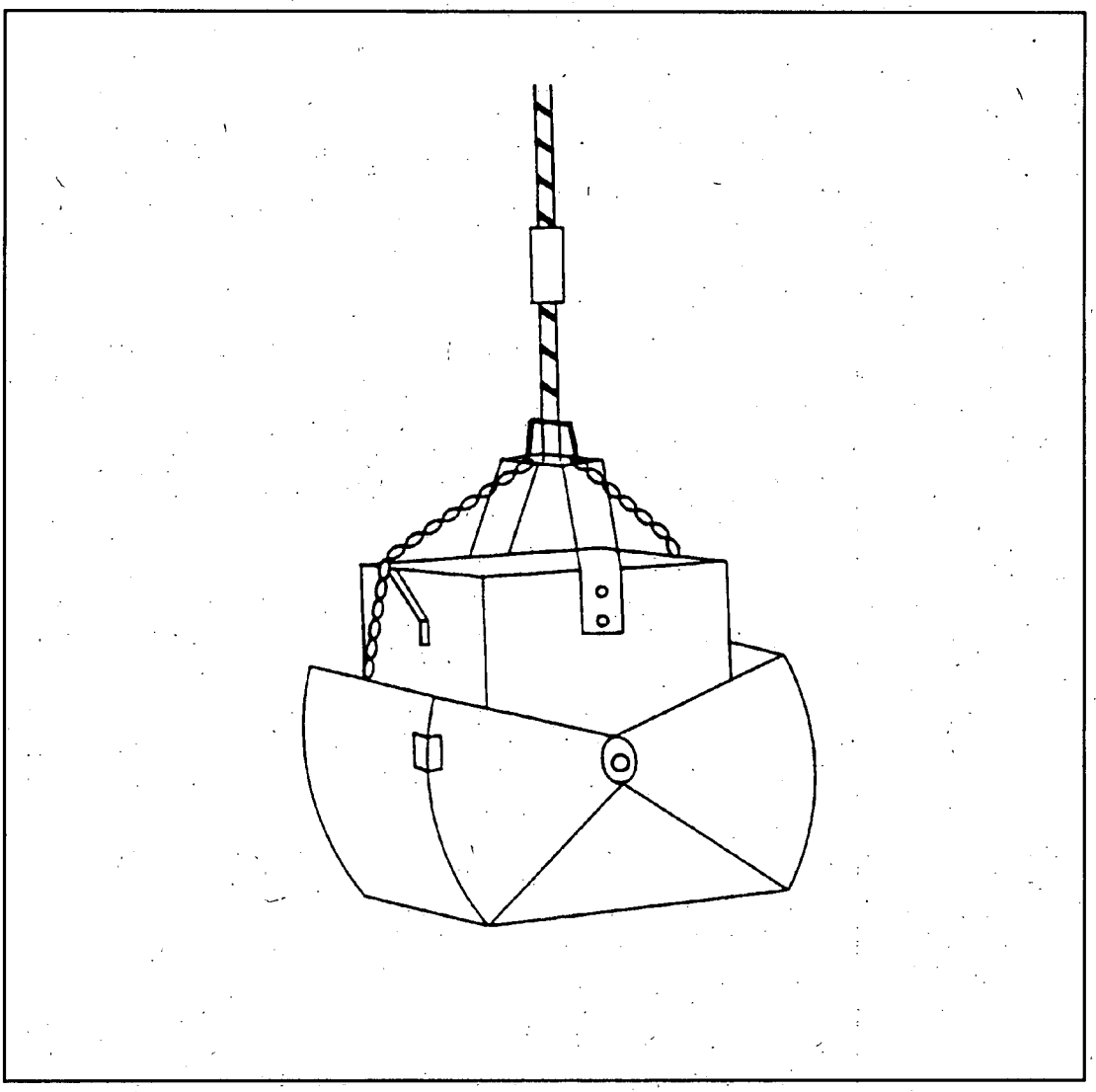
FIGURE 1. Sampling Auger



## APPENDIX A (Cont'd)

Figures

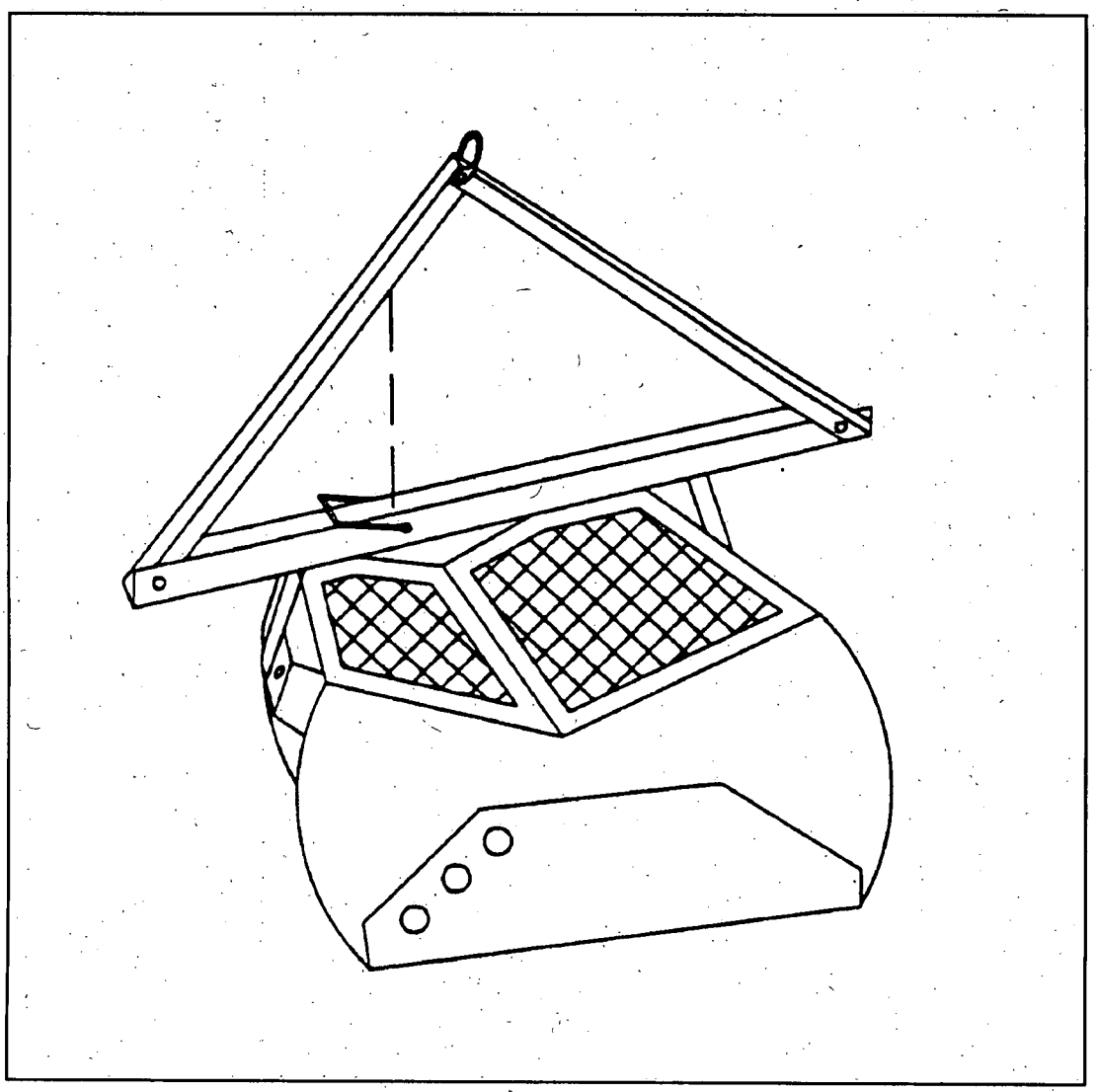
FIGURE 2. Ekman Dredge



## APPENDIX A (Cont'd)

Figures

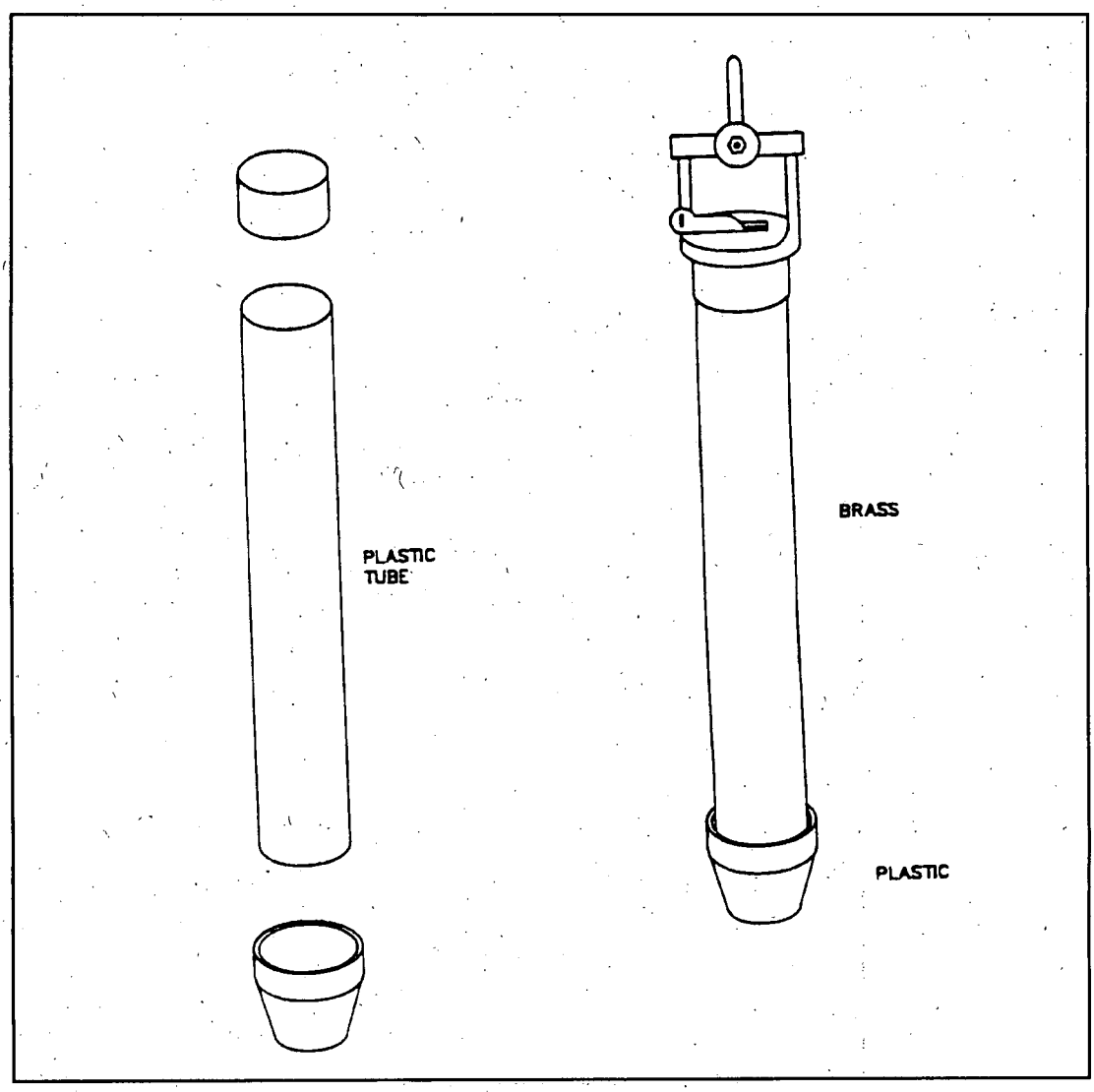
FIGURE 3. Ponar Dredge



## APPENDIX A (Cont'd)

Figures

FIGURE 4. Sample Coring Device



METHOD 6200

# FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

## 1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed below for soil and sediment samples. Some common elements are not listed in this method because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). These light elements are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed below are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF. The following RCRA analytes have been determined by this method:

| Analytes | CAS Registry No. |
|---|---|
| Antimony (Sb) | 7440-36-0 |
| Arsenic (As) | 7440-38-0 |
| Barium (Ba) | 7440-39-3 |
| Cadmium (Cd) | 7440-43-9 |
| Chromium (Cr) | 7440-47-3 |
| Cobalt (Co) | 7440-48-4 |
| Copper (Cu) | 7440-50-8 |
| Lead (Pb) | 7439-92-1 |
| Mercury (Hg) | 7439-97-6 |
| Nickel (Ni) | 7440-02-0 |
| Selenium (Se) | 7782-49-2 |
| Silver (Ag) | 7440-22-4 |
| Thallium (Tl) | 7440-28-0 |
| Tin (Sn) | 7440-31-5 |

| Analytes | CAS Registry No. |
|---|---|
| Vanadium (V) | 7440-62-2 |
| Zinc (Zn) | 7440-66-6 |

In addition, the following non-RCRA analytes have been determined by this method:

| Analytes | CAS Registry No. |
|---|---|
| Calcium (Ca) | 7440-70-2 |
| Iron (Fe) | 7439-89-6 |
| Manganese (Mn) | 7439-96-5 |
| Molybdenum (Mo) | 7439-93-7 |
| Potassium (K) | 7440-09-7 |
| Rubidium (Rb) | 7440-17-7 |
| Strontium (Sr) | 7440-24-6 |
| Thorium (Th) | 7440-29-1 |
| Titanium (Ti) | 7440-32-6 |
| Zirconium (Zr) | 7440-67-7 |

1.2 This method is a screening method to be used with confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)). This method's main strength is that it is a rapid field screening procedure. The method's lower limits of detection are typically above the toxicity characteristic regulatory level for most RCRA analytes. However, when the obtainable values for precision, accuracy, and laboratory-established sensitivity of this method meet project-specific data quality objectives (DQOs), FPXRF is a fast, powerful, cost effective technology for site characterization.

1.3 The method sensitivity or lower limit of detection depends on several factors, including the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. Example lower limits of detection for analytes of interest in environmental applications are shown in Table 1. These limits apply to a clean spiked matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (100 -600 second) count times. These sensitivity values are given for guidance only and may not always be achievable, since they will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of performance-based sensitivity is presented in Sec. 9.6.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use either sealed radioisotope sources or x-ray tubes to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples. The three electron shells include the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α), beta (β), or gamma (γ) etc., which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a $K_\alpha$ line is produced by a vacancy in the K shell filled by an L shell electron, whereas a $K_\beta$ line is produced by a vacancy in the K shell filled by an M shell electron. The $K_\alpha$ transition is on average 6 to 7 times more probable than the $K_\beta$ transition; therefore, the $K_\alpha$ line is approximately 7 times more intense than the $K_\beta$ line for a given element, making the $K_\alpha$ line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines ($L_\alpha$ and $L_\beta$) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments, specifically, in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

## 3.0 DEFINITIONS

3.1 FPXRF -- Field portable x-ray fluorescence.

3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS -- Site-specific calibration standards.

3.4 FP -- Fundamental parameter.

3.5 ROI -- Region of interest.

3.6 SRM -- Standard reference material; a standard containing certified amounts of metals in soil or sediment.

3.7 eV -- Electron volt; a unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One, Chapter Three, and the manufacturer's instructions for other definitions that may be relevant to this procedure.

## 4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup (i.e., against the cup window), the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the $K_\beta$ line of element Z-1 with the $K_\alpha$ line of element Z. This is called the $K_\alpha/K_\beta$ interference. Because the $K_\alpha$:$K_\beta$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V $K_\alpha$ and $K_\beta$ energies are 4.95 and 5.43 keV, respectively, and the Cr $K_\alpha$ energy is 5.41 keV. The Fe $K_\alpha$ and $K_\beta$ energies are 6.40 and 7.06 keV, respectively, and the Co $K_\alpha$ energy is 6.92 keV. The difference between the V $K_\beta$ and Cr $K_\alpha$ energies is 20 eV, and the difference between the Fe $K_\beta$ and the Co $K_\alpha$ energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) $K_\alpha$/lead (Pb) $L_\alpha$ and sulfur (S) $K_\alpha$/Pb $M_\alpha$. In the As/Pb case, Pb can be measured from the Pb $L_\beta$ line, and As can be measured from either the As $K_\alpha$ or the As $K_\beta$ line; in this way the interference can be corrected. If the As $K_\beta$ line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As $K_\alpha$ line. If the As $K_\alpha$ line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in reporting of a "nondetect" or a "less than" value (e.g., <300 ppm) for As, regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-

atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as Method 3050, or a total digestion procedure, such as Method 3052, is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project-specific data quality objectives (DQOs).

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method (see Table 8), the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r often exceeding 0.95, except for barium and chromium). The critical factor is that the digestion procedure and analytical reference method used should meet the DQOs of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Sec. 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10° F. The operator should follow the manufacturer's recommendations for gain check frequency.

## 5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The user is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

NOTE: No MSDS applies directly to the radiation-producing instrument because that is covered under the Nuclear Regulatory Commission (NRC) or applicable state regulations.

5.2 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operator's manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals.

Licenses for radioactive materials are of two types, specifically: (1) a general license which is usually initiated by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) a specific license which is issued to named persons for the operation of radioactive instruments as required by local, state, or federal agencies. A copy of the radioactive material license (for specific licenses only) and leak tests should be present with the instrument at all times and available to local and national authorities upon request.

X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply, however, if the tube is properly positioned within the instrument, this is only a negligible risk. Any instrument (x-ray tube or radioisotope based) is capable of delivering an electric shock from the basic circuitry when the system is inappropriately opened.

5.3 Radiation monitoring equipment should be used with the handling and operation of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs or badges should be worn in the area of maximum exposure. The maximum permissible whole-body dose from occupational exposure is 5 Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

## 6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for

use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

6.1 FPXRF spectrometer -- An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation sources -- FPXRF instruments use either a sealed radioisotope source or an x-ray tube to provide the excitation source. Many FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron Fe-55 ($^{55}$Fe), cadmium Cd-109 ($^{109}$Cd), americium Am-241 ($^{241}$Am), and curium Cm-244 ($^{244}$Cm). These sources may be contained in a probe along with a window and the detector; the probe may be connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF analysis. The decay of radioisotopes is measured in "half-lives." The half-life of a radioisotope is defined as the length of time required to reduce the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. This is due to the ever increasing time required for the analysis rather than a decrease in instrument performance. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum necessary for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of

accelerating voltage is governed both by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material and by the instrument's ability to cool the x-ray tube. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample presentation device -- FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For FPXRF instruments operated in the intrusive mode, the probe may be rotated so that the window faces either upward or downward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors -- The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide ($HgI_2$), silicon pin diode and lithium-drifted silicon Si(Li). The $HgI_2$ detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The Si(Li) detector must be cooled to at least -90 °C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a Si(Li) detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 L. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese $K_\alpha$ peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: $HgI_2$-270 eV; silicon pin diode-250 eV; Si(Li)–170 eV; and gas-filled, proportional counter-750 eV.

During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data processing units -- The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in ppm on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 3,000 to 5,000 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software built into the

units or from PCs. Once the data–storage memory of an FPXRF unit is full or at any other time, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery and battery charger.

6.3 Polyethylene sample cups -- 31 to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film -- Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 µm thick.

6.5 Mortar and pestle -- Glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers -- Glass or plastic to store samples.

6.7 Sieves -- 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels -- For smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags -- Used for collection and homogenization of soil samples.

6.10 Drying oven -- Standard convection or toaster oven, for soil and sediment samples that require drying.

## 7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Pure element standards -- Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if designated for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.3 Site-specific calibration standards -- Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.3.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of 10 samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.3.2 Each sample should be oven-dried for 2 to 4 hr at a temperature of less than 150 °C. If mercury is to be analyzed, a separate sample portion should be dried at ambient temperature as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be homogenized (see Sec. 7.3.3) and then a representative portion ground with a mortar and pestle or other mechanical means, prior to passing through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.3.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 g of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 g of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.4 Blank samples -- The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the established lower limit of detection. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.5 Standard reference materials -- Standard reference materials (SRMs) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories. When these SRMs are unavailable, alternate standards may be used (e.g., NIST 2702).

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, "Inorganic Analytes."

## 9.0 QUALITY CONTROL

9.1 Follow the manufacturer's instructions for the quality control procedures specific to use of the testing product. Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

9.2 Energy calibration check -- To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting,

which would indicate drift within the instrument. As discussed in Sec. 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (more than 10 °F).

9.2.1 The energy calibration check should be run at a frequency consistent with manufacturer's recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.2 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak. The intensity and channel number of the pure element as measured using the source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank samples -- Two types of blank samples should be analyzed for FPXRF analysis, specifically, instrument blanks and method blanks.

9.3.1 An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window. The instrument blank can be silicon dioxide, a polytetraflurorethylene (PTFE) block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the established lower limit of detection should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of detection or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration verification checks -- A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ±20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision measurements -- The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent. If both in situ and intrusive analytical techniques are used during the course of one day, it is recommended that separate precision calculations be performed for each analysis type.

The equation for calculating RSD is as follows:

$$RSD = (SD/\text{Mean Concentration}) \times 100$$

where:

RSD = Relative standard deviation for the precision measurement for the analyte
SD = Standard deviation of the concentration for the analyte
Mean concentration = Mean concentration for the analyte

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the sensitivity, but decreases sample throughput.

9.6 The lower limits of detection should be established from actual measured performance based on spike recoveries in the matrix of concern or from acceptable method performance on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity as opposed to a statistical determination based on the standard deviation of

replicate analyses of a low-concentration sample. While the statistical approach demonstrates the potential data variability for a given sample matrix at one point in time, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated. For this reason the sensitivity should be established as the lowest point of detection based on acceptable target analyte recovery in the desired sample matrix.

9.7 Confirmatory samples -- The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory samples must be splits of the well homogenized sample material. In some cases the prepared sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on project-specific data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument calibration -- Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments, namely: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental parameters calibration -- FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are necessary, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are necessary.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Sec. 7.3. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective energy FP calibration -- The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ±20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ±20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference
$C_k$ = Certified concentration of standard sample
$C_s$ = Measured concentration of standard sample

10.2.2 BFP calibration -- BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended

count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ±20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ±20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical calibration -- An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Sec. 7.3; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is necessary. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are necessary to perform an adequate empirical calibration. The exact number of standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton normalization method -- The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline reading. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton $K_{\alpha}$ peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

## 11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later during analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, remove any large or nonrepresentative debris from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Also, the soil surface must be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide example performance data for this method, this modest amount of sample preparation was found to take less than 5 min per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for in situ analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on the desired method sensitivity. Due to the heterogeneous nature of the soil sample, in situ analysis can provide only "screening" type data.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 g or 250 $cm^3$, which is enough soil to fill an 8-ounce jar. However, the exact dimensions and sample depth should take into consideration the heterogeneous deposition of contaminants and will ultimately depend on the desired project-specific data quality objectives. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Sec. 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the time necessary for homogenization procedure using the fluorescein dye ranged from 3 to 5 min per sample. As demonstrated in Secs. 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, the direct analysis through the plastic bag is possible without the more labor intensive steps of drying, grinding, and sieving given in Secs. 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps should be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 °C. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 min per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 µm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle, and sieves must be thoroughly cleaned so that any cross-contamination is below the established lower limit of detection of the procedure or DQOs of the analysis. If all recommended sample preparation steps are followed, there is a high probability the desired laboratory data quality may be obtained.

## 12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in ppm and can be downloaded to a personal computer, which can be used to provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation. See the manufacturer's instructions regarding data analysis and calculations.

## 13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The sections to follow discuss three performance evaluation factors; namely, precision, accuracy, and comparability. The example data presented in Tables 4 through 8 were generated from results obtained from six FPXRF instruments (see Sec. 13.3). The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from "nondetect" to tens of thousands of mg/kg. These data are provided for guidance purposes only.

13.3 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a $HgI_2$ detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode

detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.4 All example data presented in Tables 4 through 8 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.5 Precision measurements -- The example precision data are presented in Table 4. These data are provided for guidance purposes only. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from "nondetects" to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 4 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the lower limit of detection for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 4. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the lower limit of detection so that an RSD value calculated at 5 to 10 times this limit was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 5 shows these results. These data are provided for guidance purposes only. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the lower limit of detection for the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the in situ homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 5 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square,

measurements of different soil samples were actually taking place within the square. Table 5 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five instead of ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy measurements -- Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 6 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 6 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 6. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 6.

Table 7 provides a more detailed summary of accuracy data for one particular FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. These data are provided for guidance purposes only. Table 7 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability -- Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination ($r^2$).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 8. Similar trends in the data were seen for all instruments. These data are provided for guidance purposes only.

Table 8 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. These data are provided for guidance purposes only. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--intrusive, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not

ground; and preparation 4–intrusive, with sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with $r^2$ values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The $r^2$ values and slopes of the regression lines for barium and chromium were not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 8 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 8 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Sec. 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time necessary to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 min. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 min per sample. Lastly, when grinding and sieving is conducted, time has to be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 A. D. Hewitt, "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton $K_\alpha$ Peak Normalization Analysis," American Environmental Laboratory, pp 24-32, 1994.

13.8.2 S. Piorek and J. R. Pasmore, "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer," Third International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals, Las Vegas, Nevada, February 24-26, 1993, Vol 2, pp 1135-1151, 1993.

13.8.3 S. Shefsky, "Sample Handling Strategies for Accurate Lead-in-soil Measurements in the Field and Laboratory," *International Symposium of Field Screening Methods for Hazardous Waste and Toxic Chemicals*, Las Vegas, NV, January 29-31, 1997.

## 14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

## 15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

## 16.0 REFERENCES


1. Metorex, X-MET 920 User's Manual.

2. Spectrace Instruments, "Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction," 1994.

3. TN Spectrace, Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.

4. Unpublished SITE data, received from PRC Environment Management, Inc.


## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE INTERFERENCE FREE LOWER LIMITS OF DETECTION

| Analyte | Chemical Abstract Series Number | Lower Limit of Detection in Quartz Sand (milligrams per kilogram) |
|---|---|---|
| Antimony (Sb) | 7440-36-0 | 40 |
| Arsenic (As) | 7440-38-0 | 40 |
| Barium (Ba) | 7440-39-3 | 20 |
| Cadmium (Cd) | 7440-43-9 | 100 |
| Calcium (Ca) | 7440-70-2 | 70 |
| Chromium (Cr) | 7440-47-3 | 150 |
| Cobalt (Co) | 7440-48-4 | 60 |
| Copper (Cu) | 7440-50-8 | 50 |
| Iron (Fe) | 7439-89-6 | 60 |
| Lead (Pb) | 7439-92-1 | 20 |
| Manganese (Mn) | 7439-96-5 | 70 |
| Mercury (Hg) | 7439-97-6 | 30 |
| Molybdenum (Mo) | 7439-93-7 | 10 |
| Nickel (Ni) | 7440-02-0 | 50 |
| Potassium (K) | 7440-09-7 | 200 |
| Rubidium (Rb) | 7440-17-7 | 10 |
| Selenium (Se) | 7782-49-2 | 40 |
| Silver (Ag) | 7440-22-4 | 70 |
| Strontium (Sr) | 7440-24-6 | 10 |
| Thallium (Tl) | 7440-28-0 | 20 |
| Thorium (Th) | 7440-29-1 | 10 |
| Tin (Sn) | 7440-31-5 | 60 |
| Titanium (Ti) | 7440-32-6 | 50 |
| Vanadium (V) | 7440-62-2 | 50 |
| Zinc (Zn) | 7440-66-6 | 50 |
| Zirconium (Zr) | 7440-67-7 | 10 |

Source: Refs. 1, 2, and 3
These data are provided for guidance purposes only.

TABLE 2

SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS

| Source | Activity (mCi) | Half-Life (Years) | Excitation Energy (keV) | Elemental Analysis Range | |
|---|---|---|---|---|---|
| Fe-55 | 20-50 | 2.7 | 5.9 | Sulfur to Chromium<br>Molybdenum to Barium | K Lines<br>L Lines |
| Cd-109 | 5-30 | 1.3 | 22.1 and 87.9 | Calcium to Rhodium<br>Tantalum to Lead<br>Barium to Uranium | K Lines<br>K Lines<br>L Lines |
| Am-241 | 5-30 | 432 | 26.4 and 59.6 | Copper to Thulium<br>Tungsten to Uranium | K Lines<br>L Lines |
| Cm-244 | 60-100 | 17.8 | 14.2 | Titanium to Selenium<br>Lanthanum to Lead | K Lines<br>L Lines |

Source: Refs. 1, 2, and 3

TABLE 3

SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS

| Anode Material | Recommended Voltage Range (kV) | K-alpha Emission (keV) | Elemental Analysis Range | |
|---|---|---|---|---|
| Cu | 18-22 | 8.04 | Potassium to Cobalt<br>Silver to Gadolinium | K Lines<br>L Lines |
| Mo | 40-50 | 17.4 | Cobalt to Yttrium<br>Europium to Radon | K Lines<br>L Lines |
| Ag | 50-65 | 22.1 | Zinc to Technicium<br>Ytterbium to Neptunium | K Lines<br>L Lines |

Source: Ref. 4

Notes: The sample elements excited are chosen by taking as the lower limit the same ratio of excitation line energy to element absorption edge as in Table 2 (approximately 0.45) and the requirement that the excitation line energy be above the element absorption edge as the upper limit (L2 edges used for L lines). K-beta excitation lines were ignored.

TABLE 4

EXAMPLE PRECISION VALUES

| Analyte | Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the Lower Limit of Detection | | | | | |
|---|---|---|---|---|---|---|
| | TN 9000 | TN Lead Analyzer | X-MET 920 (SiLi Detector) | X-MET 920 (Gas-Filled Detector) | XL Spectrum Analyzer | MAP Spectrum Analyzer |
| Antimony | 6.54 | NR | NR | NR | NR | NR |
| Arsenic | 5.33 | 4.11 | 3.23 | 1.91 | 12.47 | 6.68 |
| Barium | 4.02 | NR | 3.31 | 5.91 | NR | NR |
| Cadmium | 29.84[a] | NR | 24.80[a] | NR | NR | NR |
| Calcium | 2.16 | NR | NR | NR | NR | NR |
| Chromium | 22.25 | 25.78 | 22.72 | 3.91 | 30.25 | NR |
| Cobalt | 33.90 | NR | NR | NR | NR | NR |
| Copper | 7.03 | 9.11 | 8.49 | 9.12 | 12.77 | 14.86 |
| Iron | 1.78 | 1.67 | 1.55 | NR | 2.30 | NR |
| Lead | 6.45 | 5.93 | 5.05 | 7.56 | 6.97 | 12.16 |
| Manganese | 27.04 | 24.75 | NR | NR | NR | NR |
| Molybdenum | 6.95 | NR | NR | NR | 12.60 | NR |
| Nickel | 30.85[a] | NR | 24.92[a] | 20.92[a] | NA | NR |
| Potassium | 3.90 | NR | NR | NR | NR | NR |
| Rubidium | 13.06 | NR | NR | NR | 32.69[a] | NR |
| Strontium | 4.28 | NR | NR | NR | 8.86 | NR |
| Tin | 24.32[a] | NR | NR | NR | NR | NR |
| Titanium | 4.87 | NR | NR | NR | NR | NR |
| Zinc | 7.27 | 7.48 | 4.26 | 2.28 | 10.95 | 0.83 |
| Zirconium | 3.58 | NR | NR | NR | 6.49 | NR |

These data are provided for guidance purposes only.
Source: Ref. 4

[a] These values are biased high because the concentration of these analytes in the soil samples was near the lower limit of detection for that particular FPXRF instrument.

NR Not reported.

NA Not applicable; analyte was reported but was below the established lower limit detection.

TABLE 5

EXAMPLES OF PRECISION AS AFFECTED BY SAMPLE PREPARATION

| Analyte | Average Relative Standard Deviation for Each Preparation Method | | |
|---|---|---|---|
| | In Situ-Field | Intrusive-Undried and Unground | Intrusive-Dried and Ground |
| Antimony | 30.1 | 15.0 | 14.4 |
| Arsenic | 22.5 | 5.36 | 3.76 |
| Barium | 17.3 | 3.38 | 2.90 |
| Cadmium[a] | 41.2 | 30.8 | 28.3 |
| Calcium | 17.5 | 1.68 | 1.24 |
| Chromium | 17.6 | 28.5 | 21.9 |
| Cobalt | 28.4 | 31.1 | 28.4 |
| Copper | 26.4 | 10.2 | 7.90 |
| Iron | 10.3 | 1.67 | 1.57 |
| Lead | 25.1 | 8.55 | 6.03 |
| Manganese | 40.5 | 12.3 | 13.0 |
| Mercury | ND | ND | ND |
| Molybdenum | 21.6 | 20.1 | 19.2 |
| Nickel[a] | 29.8 | 20.4 | 18.2 |
| Potassium | 18.6 | 3.04 | 2.57 |
| Rubidium | 29.8 | 16.2 | 18.9 |
| Selenium | ND | 20.2 | 19.5 |
| Silver[a] | 31.9 | 31.0 | 29.2 |
| Strontium | 15.2 | 3.38 | 3.98 |
| Thallium | 39.0 | 16.0 | 19.5 |
| Thorium | NR | NR | NR |
| Tin | ND | 14.1 | 15.3 |
| Titanium | 13.3 | 4.15 | 3.74 |
| Vanadium | NR | NR | NR |
| Zinc | 26.6 | 13.3 | 11.1 |
| Zirconium | 20.2 | 5.63 | 5.18 |

These data are provided for guidance purposes only.
Source: Ref. 4
[a] These values may be biased high because the concentration of these analytes in the soil samples was near the lower limit of detection.
ND Not detected.
NR Not reported.

TABLE 6

EXAMPLE ACCURACY VALUES

| Analyte | Instrument | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TN 9000 | | | | TN Lead Analyzer | | | | X-MET 920 (SiLi Detector) | | | | XL Spectrum Analyzer | | | |
| | n | Range of % Rec. | Mean % Rec. | SD | n | Range of % Rec. | Mean % Rec. | SD | n | Range of % Rec. | Mean % Rec | SD | n | Range of % Rec. | Mean % Rec. | SD |
| Sb | 2 | 100-149 | 124.3 | NA | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| As | 5 | 68-115 | 92.8 | 17.3 | 5 | 44-105 | 83.4 | 23.2 | 4 | 9.7-91 | 47.7 | 39.7 | 5 | 38-535 | 189.8 | 206 |
| Ba | 9 | 98-198 | 135.3 | 36.9 | -- | -- | -- | -- | 9 | 18-848 | 168.2 | 262 | -- | -- | -- | -- |
| Cd | 2 | 99-129 | 114.3 | NA | -- | -- | -- | -- | 6 | 81-202 | 110.5 | 45.7 | -- | -- | -- | -- |
| Cr | 2 | 99-178 | 138.4 | NA | -- | -- | -- | -- | 7 | 22-273 | 143.1 | 93.8 | 3 | 98-625 | 279.2 | 300 |
| Cu | 8 | 61-140 | 95.0 | 28.8 | 6 | 38-107 | 79.1 | 27.0 | 11 | 10-210 | 111.8 | 72.1 | 8 | 95-480 | 203.0 | 147 |
| Fe | 6 | 78-155 | 103.7 | 26.1 | 6 | 89-159 | 102.3 | 28.6 | 6 | 48-94 | 80.4 | 16.2 | 6 | 26-187 | 108.6 | 52.9 |
| Pb | 11 | 66-138 | 98.9 | 19.2 | 11 | 68-131 | 97.4 | 18.4 | 12 | 23-94 | 72.7 | 20.9 | 13 | 80-234 | 107.3 | 39.9 |
| Mn | 4 | 81-104 | 93.1 | 9.70 | 3 | 92-152 | 113.1 | 33.8 | -- | -- | -- | -- | -- | -- | -- | -- |
| Ni | 3 | 99-122 | 109.8 | 12.0 | -- | -- | -- | -- | -- | -- | -- | -- | 3 | 57-123 | 87.5 | 33.5 |
| Sr | 8 | 110-178 | 132.6 | 23.8 | -- | -- | -- | -- | -- | -- | -- | -- | 7 | 86-209 | 125.1 | 39.5 |
| Zn | 11 | 41-130 | 94.3 | 24.0 | 10 | 81-133 | 100.0 | 19.7 | 12 | 46-181 | 106.6 | 34.7 | 11 | 31-199 | 94.6 | 42.5 |

Source: Ref. 4. These data are provided for guidance purposes only.
n: Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.
SD: Standard deviation; NA: Not applicable; only two data points, therefore, a SD was not calculated.
%Rec.: Percent recovery.
-- No data.

TABLE 7

EXAMPLE ACCURACY FOR TN 9000[a]

| Standard Reference Material | Arsenic | | | Barium | | | Copper | | | Lead | | | Zinc | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. | Cert. Conc. | Meas. Conc. | %Rec. |
| RTC CRM-021 | 24.8 | ND | NA | 586 | 1135 | 193.5 | 4792 | 2908 | 60.7 | 144742 | 149947 | 103.6 | 546 | 224 | 40.9 |
| RTC CRM-020 | 397 | 429 | 92.5 | 22.3 | ND | NA | 753 | 583 | 77.4 | 5195 | 3444 | 66.3 | 3022 | 3916 | 129.6 |
| BCR CRM 143R | -- | -- | -- | -- | -- | -- | 131 | 105 | 80.5 | 180 | 206 | 114.8 | 1055 | 1043 | 99.0 |
| BCR CRM 141 | -- | -- | -- | -- | -- | -- | 32.6 | ND | NA | 29.4 | ND | NA | 81.3 | ND | NA |
| USGS GXR-2 | 25.0 | ND | NA | 2240 | 2946 | 131.5 | 76.0 | 106 | 140.2 | 690 | 742 | 107.6 | 530 | 596 | 112.4 |
| USGS GXR-6 | 330 | 294 | 88.9 | 1300 | 2581 | 198.5 | 66.0 | ND | NA | 101 | 80.9 | 80.1 | 118 | ND | NA |
| NIST 2711 | 105 | 104 | 99.3 | 726 | 801 | 110.3 | 114 | ND | NA | 1162 | 1172 | 100.9 | 350 | 333 | 94.9 |
| NIST 2710 | 626 | 722 | 115.4 | 707 | 782 | 110.6 | 2950 | 2834 | 96.1 | 5532 | 5420 | 98.0 | 6952 | 6476 | 93.2 |
| NIST 2709 | 17.7 | ND | NA | 968 | 950 | 98.1 | 34.6 | ND | NA | 18.9 | ND | NA | 106 | 98.5 | 93.0 |
| NIST 2704 | 23.4 | ND | NA | 414 | 443 | 107.0 | 98.6 | 105 | 106.2 | 161 | 167 | 103.5 | 438 | 427 | 97.4 |
| CNRC PACS-1 | 211 | 143 | 67.7 | -- | 772 | NA | 452 | 302 | 66.9 | 404 | 332 | 82.3 | 824 | 611 | 74.2 |
| SARM-51 | -- | -- | -- | 335 | 466 | 139.1 | 268 | 373 | 139.2 | 5200 | 7199 | 138.4 | 2200 | 2676 | 121.6 |
| SARM-52 | -- | -- | -- | 410 | 527 | 128.5 | 219 | 193 | 88.1 | 1200 | 1107 | 92.2 | 264 | 215 | 81.4 |

Source: Ref. 4. These data are provided for guidance purposes only.

[a] All concentrations in milligrams per kilogram.

%Rec.: Percent recovery; ND: Not detected; NA: Not applicable.

-- No data.

TABLE 8

EXAMPLE REGRESSION PARAMETERS FOR COMPARABILITY[1]

| | Arsenic | | | | Barium | | | | Copper | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope |
| All Data | 824 | 0.94 | 1.62 | 0.94 | 1255 | 0.71 | 60.3 | 0.54 | 984 | 0.93 | 2.19 | 0.93 |
| Soil 1 | 368 | 0.96 | 1.41 | 0.95 | 393 | 0.05 | 42.6 | 0.11 | 385 | 0.94 | 1.26 | 0.99 |
| Soil 2 | 453 | 0.94 | 1.51 | 0.96 | 462 | 0.56 | 30.2 | 0.66 | 463 | 0.92 | 2.09 | 0.95 |
| Soil 3 | — | — | — | — | 400 | 0.85 | 44.7 | 0.59 | 136 | 0.46 | 16.60 | 0.57 |
| Prep 1 | 207 | 0.87 | 2.69 | 0.85 | 312 | 0.64 | 53.7 | 0.55 | 256 | 0.87 | 3.89 | 0.87 |
| Prep 2 | 208 | 0.97 | 1.38 | 0.95 | 315 | 0.67 | 64.6 | 0.52 | 246 | 0.96 | 2.04 | 0.93 |
| Prep 3 | 204 | 0.96 | 1.20 | 0.99 | 315 | 0.78 | 64.6 | 0.53 | 236 | 0.97 | 1.45 | 0.99 |
| Prep 4 | 205 | 0.96 | 1.45 | 0.98 | 313 | 0.81 | 58.9 | 0.55 | 246 | 0.96 | 1.99 | 0.96 |

| | Lead | | | | Zinc | | | | Chromium | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope | n | $r^2$ | Int. | Slope |
| All Data | 1205 | 0.92 | 1.66 | 0.95 | 1103 | 0.89 | 1.86 | 0.95 | 280 | 0.70 | 64.6 | 0.42 |
| Soil 1 | 357 | 0.94 | 1.41 | 0.96 | 329 | 0.93 | 1.78 | 0.93 | — | — | — | — |
| Soil 2 | 451 | 0.93 | 1.62 | 0.97 | 423 | 0.85 | 2.57 | 0.90 | — | — | — | — |
| Soil 3 | 397 | 0.90 | 2.40 | 0.90 | 351 | 0.90 | 1.70 | 0.98 | 186 | 0.66 | 38.9 | 0.50 |
| Prep 1 | 305 | 0.80 | 2.88 | 0.86 | 286 | 0.79 | 3.16 | 0.87 | 105 | 0.80 | 66.1 | 0.43 |
| Prep 2 | 298 | 0.97 | 1.41 | 0.96 | 272 | 0.95 | 1.86 | 0.93 | 77 | 0.51 | 81.3 | 0.36 |
| Prep 3 | 302 | 0.98 | 1.26 | 0.99 | 274 | 0.93 | 1.32 | 1.00 | 49 | 0.73 | 53.7 | 0.45 |
| Prep 4 | 300 | 0.96 | 1.38 | 1.00 | 271 | 0.94 | 1.41 | 1.01 | 49 | 0.75 | 31.6 | 0.56 |

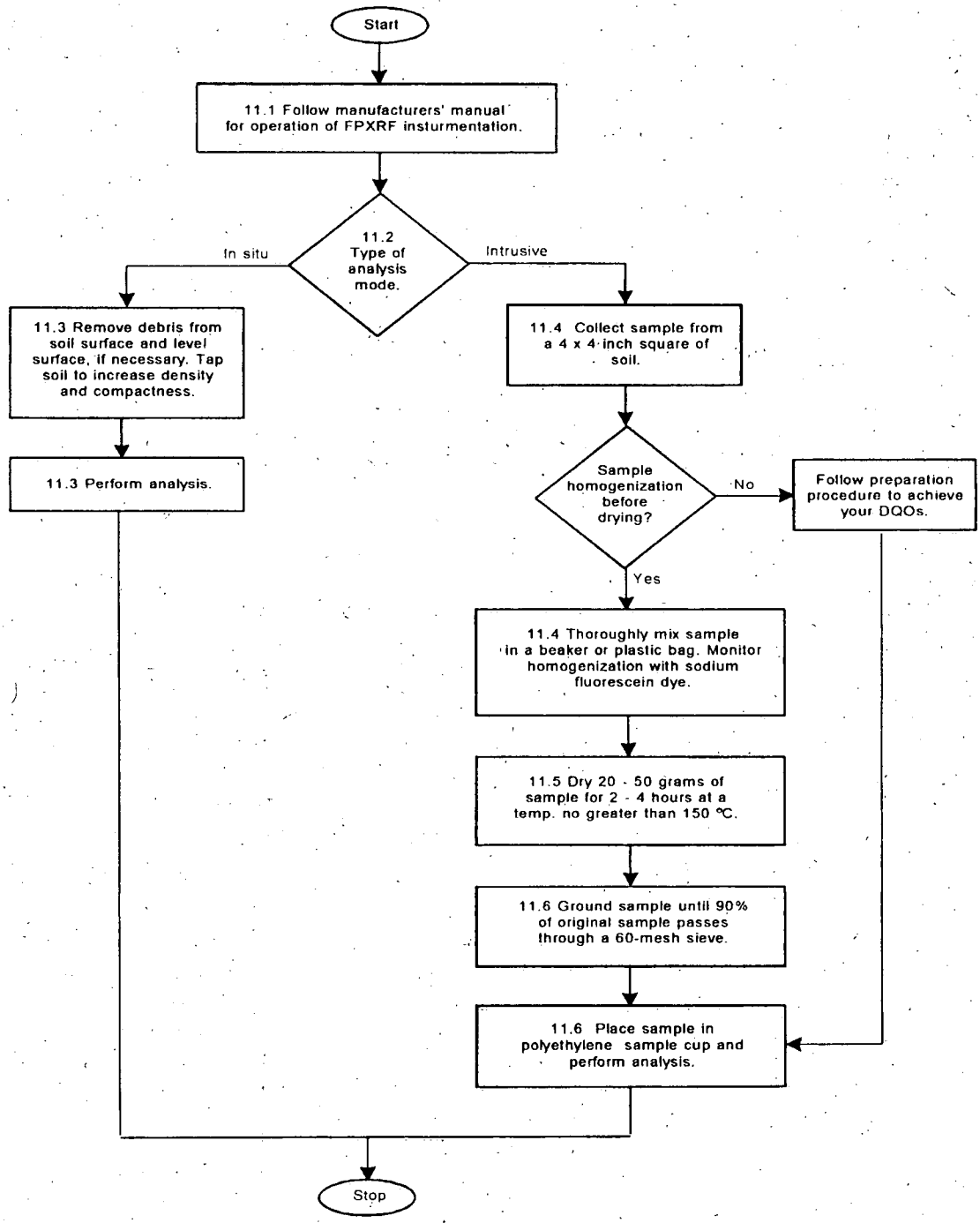
Source: Ref. 4. These data are provided for guidance purposes only.

[1] Log-transformed data

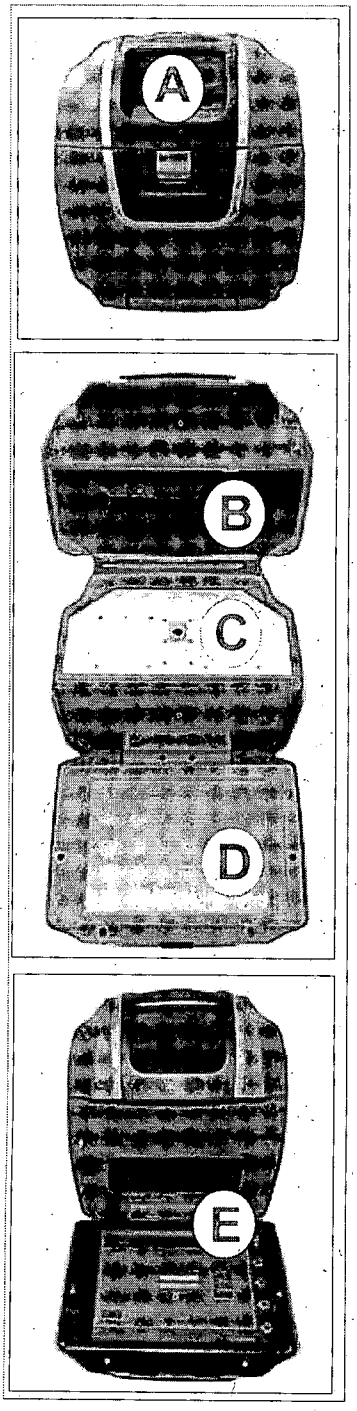
n: Number of data points; $r^2$: Coefficient of determination; Int.: Y-intercept

— No applicable data

# FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT



# 1. Introduction and System Tour




***Getting Started* includes:**

- Tour of the system noting all major components.
- Instructions for these tasks...



## Tour of the *X-50 Mobile XRF* System

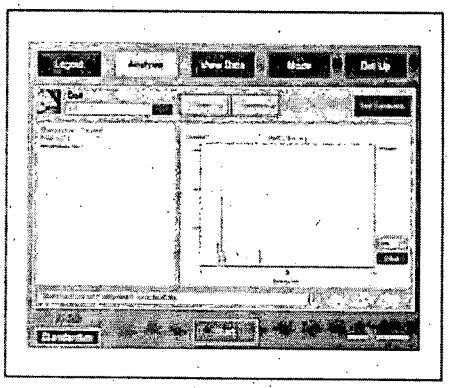
A. **Molded enclosure** that forms a portable, radiation-safe test chamber.

B. **Hinged lid** with safety interlocks to ensure a closed beam system. Handle contains high intensity safety indicator lights.

C. **Main chassis** with test platform and Kapton measurement window.
- Chassis also contains sub-systems for...
  - Excitation including multibeam capability
  - Detection
  - Safety Interlocks
  - Input/Output (I/O) Panel

D. **Computer**, industrial style, including:
- A completely integrated package featuring...
  - Licensed Windows® XP Embedded Runtime software.
  - Folding panel with touch-screen I/O with consolidated keyboard function.

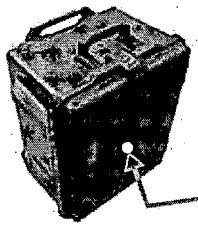
E. **Application Software**
- Easy operations with InnovX Version 2.0 User Interface
- Extensive sample identification and analysis.
- Fast results that can be viewed or saved.
- Major modes include...
  - Soil (multibeam options)
  - Mining
  - Analytical



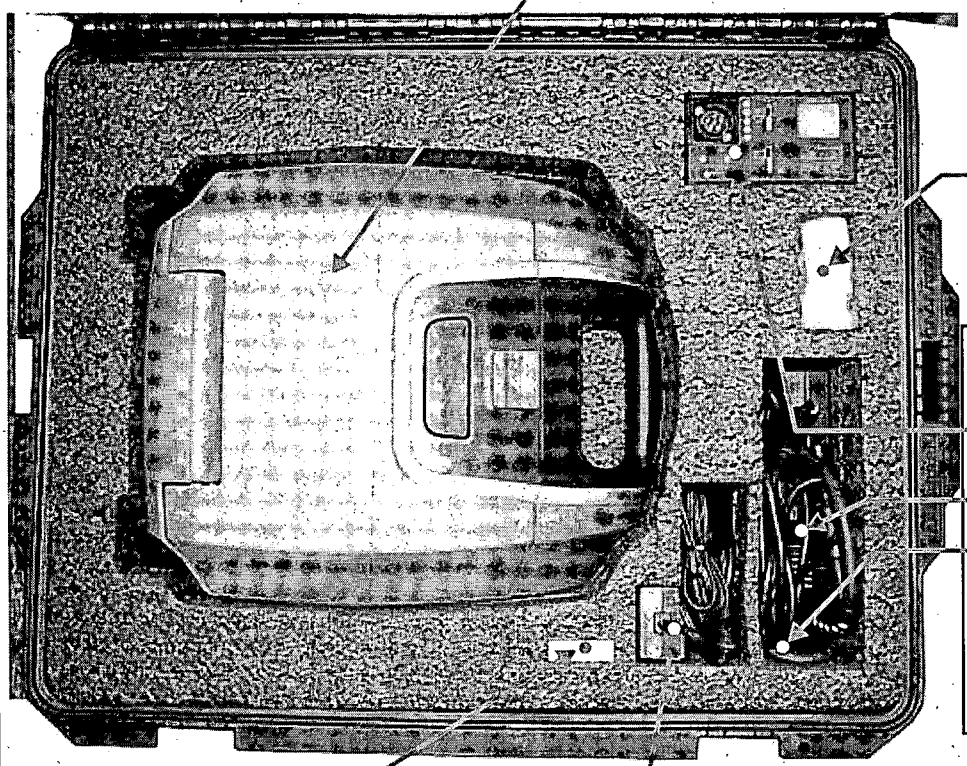
# 2. Unpack the Instrument

The X-50 analyzer and its accessories are shipped in an industrial carry case.
Use these steps to unpack the system:

1. Remove carry case from shipping carton.
2. Open the carry case and remove the X-50 instrument and all accessories.
3. Look for obvious damage to the parts.
4. Immediately report any problems to Innov-X.



## ITEM CHECKLIST for Innov-X Systems X-50 Mobile XRF Analyzer



- ❒ Industrial Carry Case
- ❒ X-50 Analyzer
- ❒ Reference Samples

***Optional Accessories***

- ❒ Li-Ion Battery
- ❒ Battery Charger Assembly
- ❒ Interconnect Cable
- ❒ Sample Holder/Guide (not shown)

- ❒ Standardization Coupon
- ❒ AC Power Adapter (for X-50)
- ❒ End User Documentation incl. S/W License (not shown)

# 3. Hardware Setup

When the X-50 is removed from its carrying case it is "ready to run."
**No assembly is required.**
However, there are physical and cabling considerations.

## a. Physical Planning

– Where will the instrument be used?

It weighs about 26 pounds (11 kilograms). It can sit on a lab table (inside) or on the ground (outside at field sites).

– What precautions must be observed for outdoor use?

Do not operate it in the rain.

The unit can be operated when sitting at an angle. If the sample remains stationary over the measurement window and the lid closes properly, the test can proceed.

– How much space (area) to allocate?

To make a minimum footprint, add at least 6 inches beyond the actual 12.5" width. Plan on a 27" span front-to-back when the lid and computer panel are open.

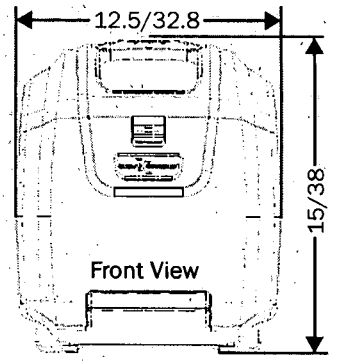
• Ensure that the cooling vents are not obstructed.

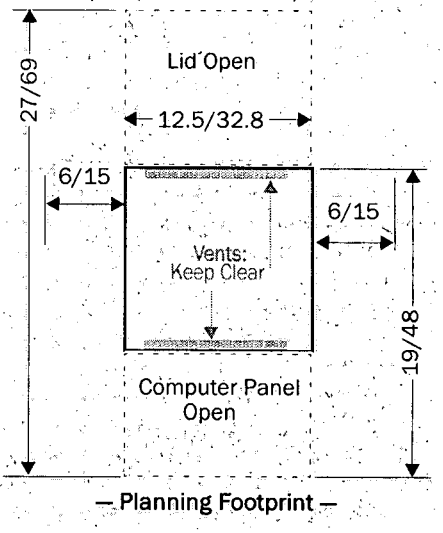
– Any special space issues for height?

The computer/monitor has a touchscreen input. Operator must be able to access the screen comfortably and reliably.

– What are the electrical power requirements?

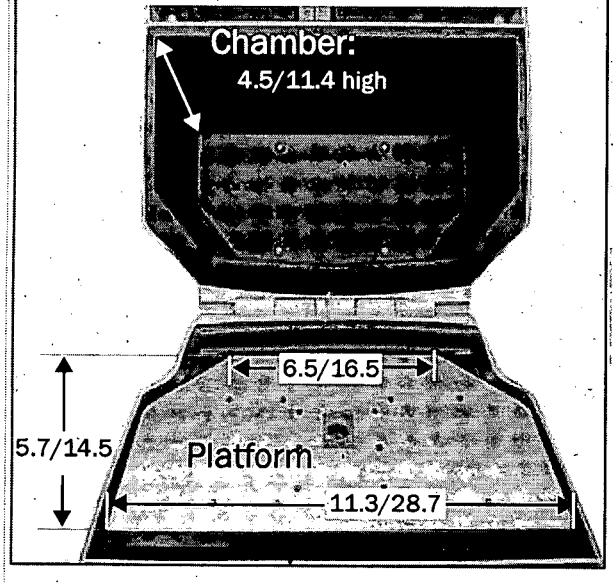
Minimal – Less than 70 watts draw.

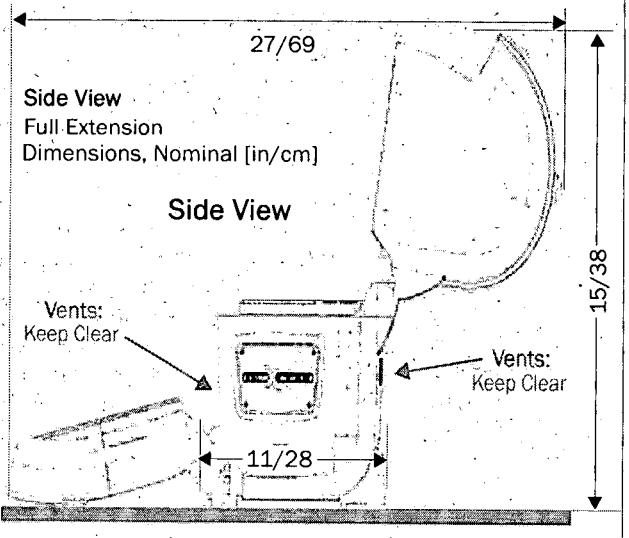


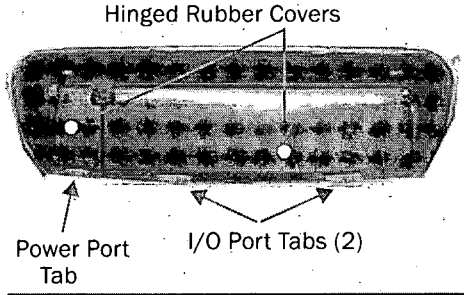

– Planning Footprint –

Prior to measuring a sample, note the dimensions of the test chamber/platform.
Ensure that the Lid can close completely



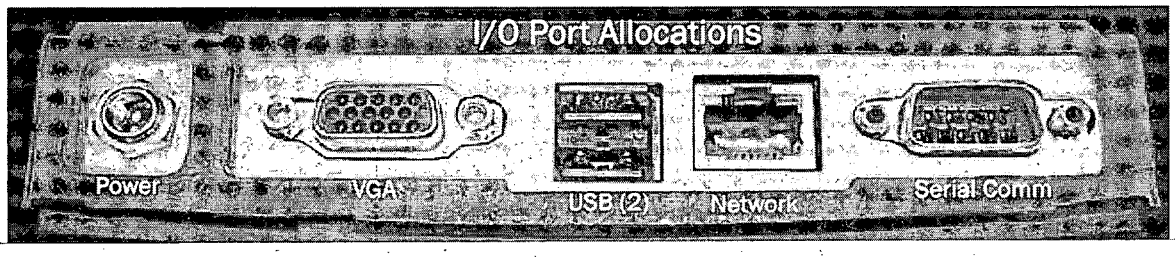



## b. Cable Connections




Lift the hinged rubber covers from the Power port and I/O panel located on the lower rear of the unit to reveal:

- **Power** port for AC Power adapter or Battery cable input.
- **VGA port** to attach an external monitor.
- **USB ports (2)** can be used for...
  - Local data storage via flash memory device.
  - External keyboard
  - External mouse
- **RJ45 socket** for network access (hardwired).
- **Serial Comm** port to attach external devices.



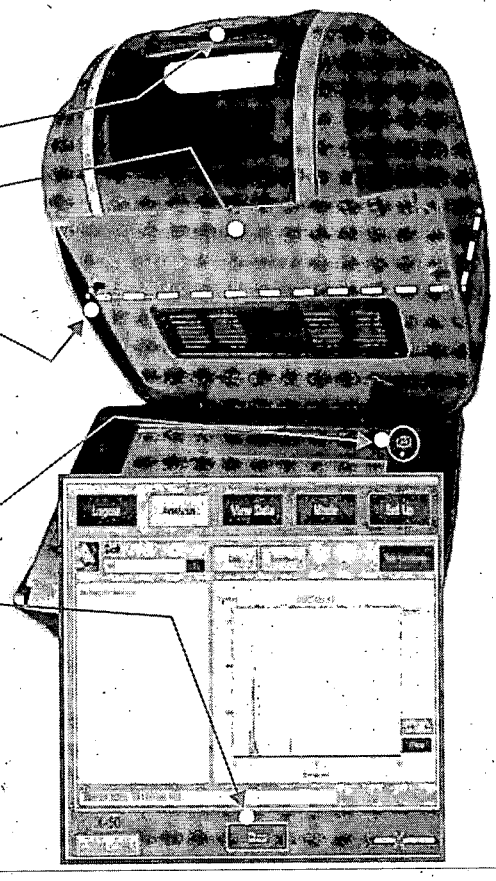

# 4.Safety Features

## a. Hardware

| | |
|---|---|
| X-Ray Indicator Handle | Three high intensity red LEDs glow when the X-ray beam is ON |
| Shielding | Entire test chamber (lid and measurement platform) is shielded. |
| Interlock Sensors | Lid interlocks ensure lid is closed prior to X-rays turning ON. Interrupts beam (X-rays OFF) if lid is lifted during an active test. |

## b. Emergency Shutoff

| | |
|---|---|
| Membrane Switch | Press and hold **I/O** switch; entire unit shuts down within 5 seconds. |
| **STOP** button on User Interface (UI) | Press **STOP** button on UI to terminate X-ray beam immediately. |
| Power Cord | Pull Power adapter cord from unit; entire unit immediately shuts down |

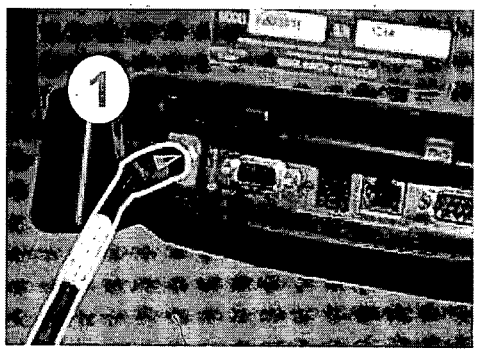


# 5. Operations

## Typical Startup Sequence

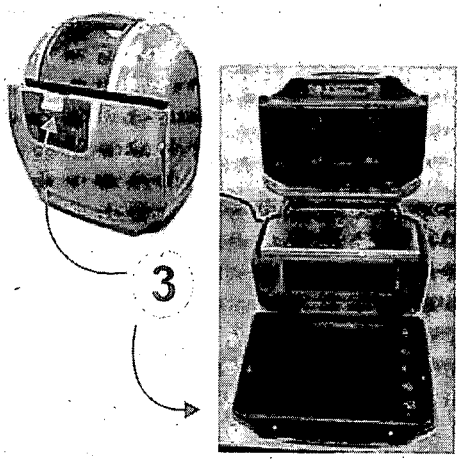
1. Plug in power using the AC adapter or battery.
2. Set up other I/O conditions such as cabling alternatives, memory card, et al, for your needs
3. Pull the blue latch down and gently swing the touchscreen computer panel out and down.

> **TIP** Support the panel on the same horizontal surface (bench or desk) as the main body of the X-50.

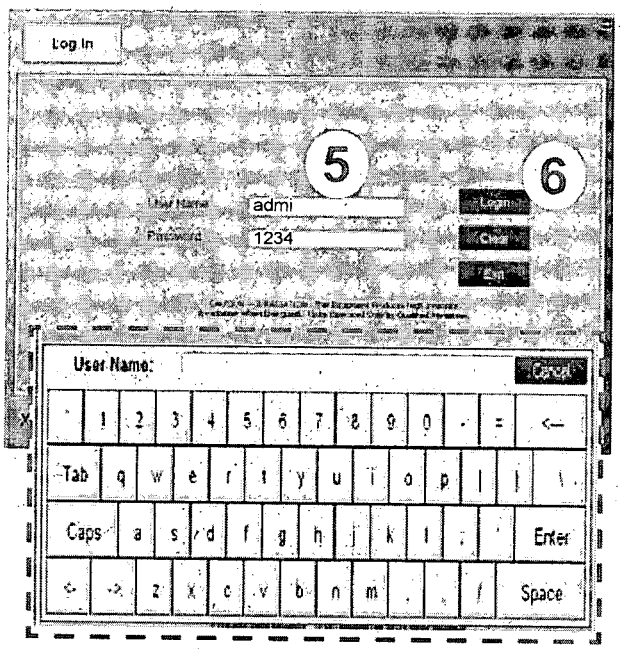


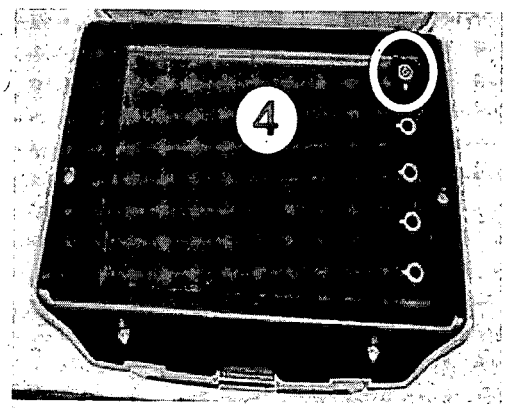

4. Turn on computer with the button (membrane switch) in the upper right corner.
   - Green LED comes on;
   - Windows® XP Embedded Runtime loads;
   - Electronic circuitry (including fans) comes on;
   - The X-50 Version 2.0 User Interface (UI) loads.
5. Enter your *User Name* and *Password*
   Touch each blank field to call the virtual keyboard

> **TIP** The default information is:
> *User Name* --> **admi**
> *Password* ---> **1234**

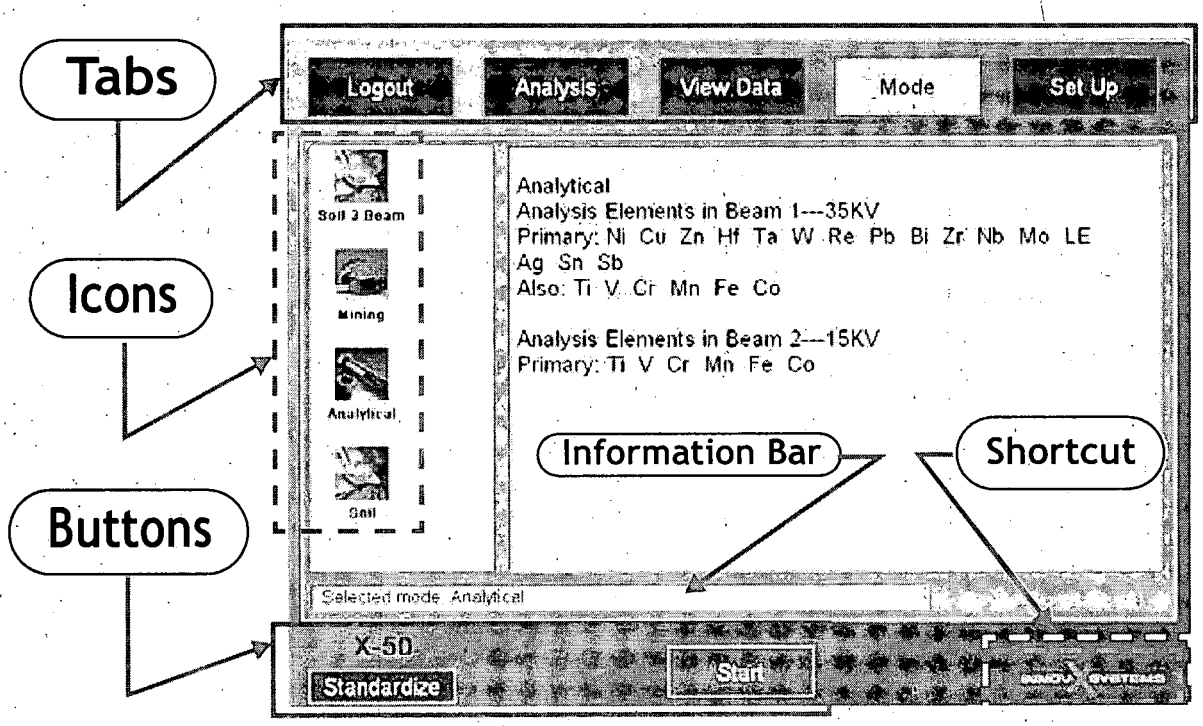



6. Press the ***Login*** button



## Navigating the Ver. 2.0 User Interface (2.0_UI)

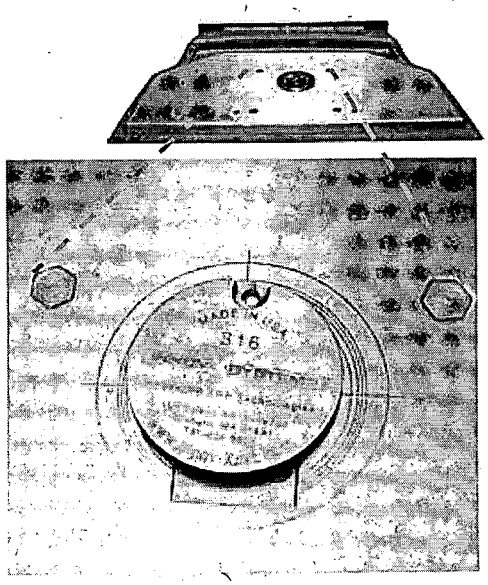



### Selecting Your Mode

By default the instrument starts up in the **last used** mode. If this is your desired current mode, continue with a Standardization or some other operation.
To change modes,

1. Press the Mode tab to invoke the screen shown above.
2. Choose your desired mode by selecting the appropriate Icon.

> **TIP** • An external keyboard and mouse may be applied via the USB ports.



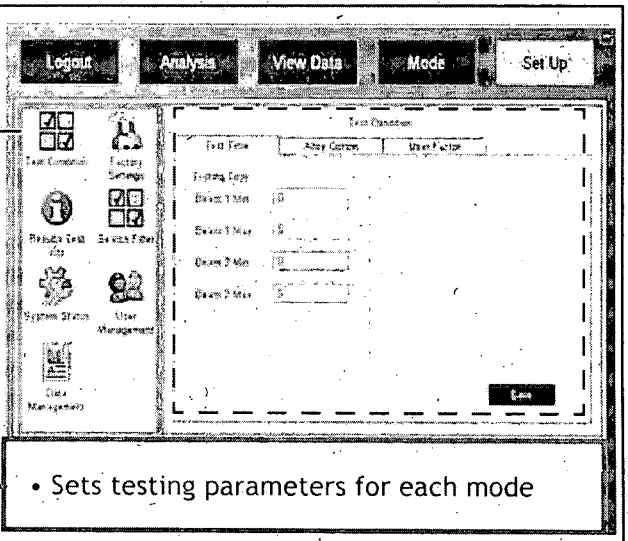
### Standardizing the Unit

1. Open the lid and place the Standardization Coupon over the measuring widow;
   – Ensure that it completely covers the window.
2. Close the lid.
3. Press *Standardize* on current 2.0_UI screen.
   The Information Bar reports the progress of the operation.
4. After completing successfully, open the lid and remove the Standardization Coupon.

## Using the Set Up Facilities

The SETUP tab introduces several facilities.

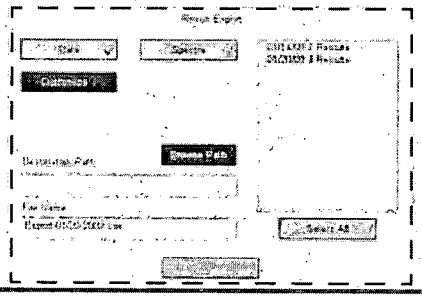
Select an Icon to call the desired screen.




• Sets testing parameters for each mode

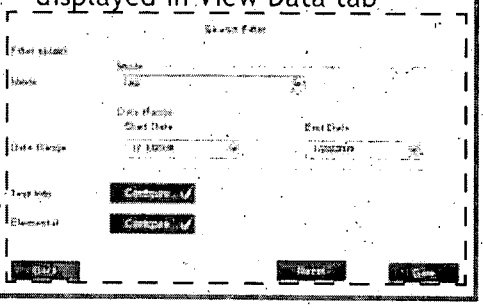
Data Management

• Configure and export results



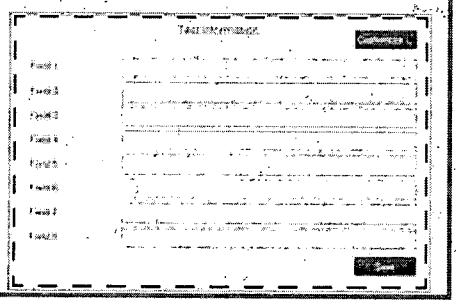
Search Filter

• Set parameters to narrow results displayed in View Data tab



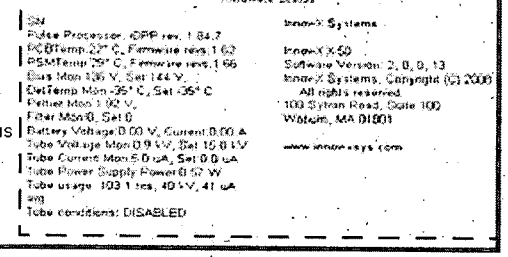
Results Test Info

• Configures user entered information fields.



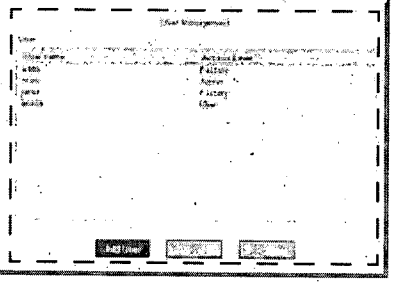
System Status

• Displays hardware & software status



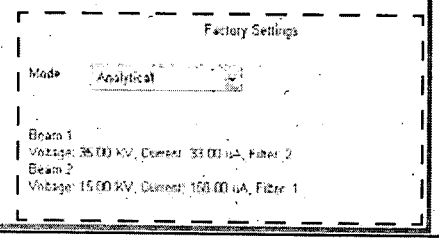
User Management

• Change Users/Passwords



Factory Settings

• No user functions available

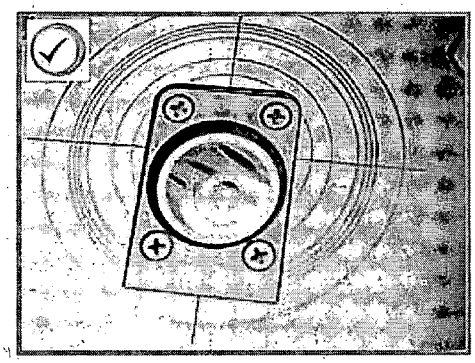


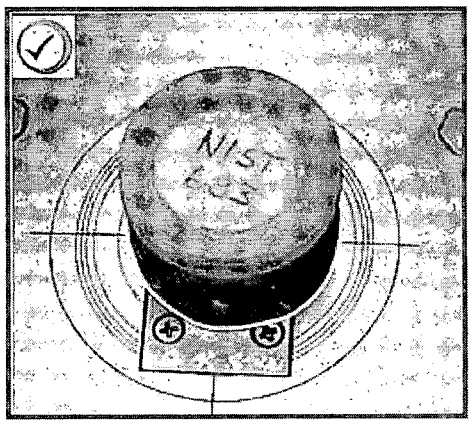
## Conducting a Test

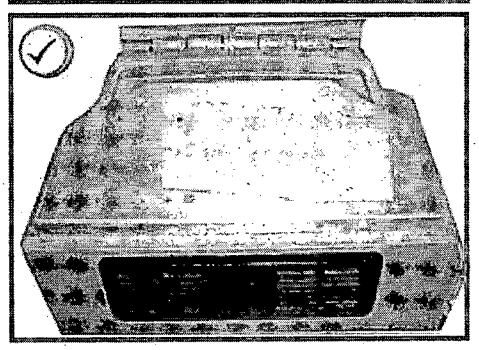
1. Open lid.
2. Place sample over the measurement window.

### TIPS

- **USE** the platform's engraved alignment rings and cross-hairs to position a test specimen for **accurate** and **repeatable** readings.
- When using sample cups, ensure that they are **FULL**.
- When employing a plastic bag to measure soil samples...
  - Arrange bag material so that at least a 2 cm thickness is over the window.
  - Try to use bags with very thin walls (low cost "store brands" are better than national brands)





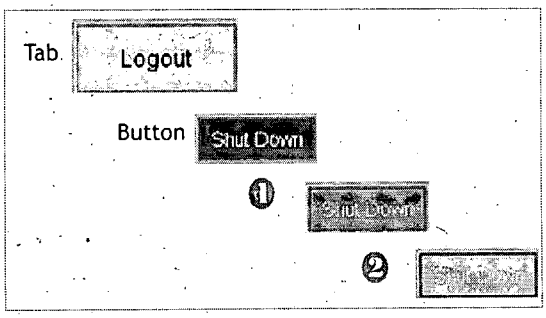



3. Close the lid.
4. Select *Start*
5. Testing begins, test status is displayed in Information Bar
   Results are available in several ways...
   a. Visually on Analysis screen.
   b. Saved to default internal hard disk.
   c. Exported to USB flash memory or network drive for later reporting and analysis.

## Shutdown Procedures

The recommended shutdown procedure is:

- Go to Logout Tab
  Double touch the *Shutdown* button
  - First press ① causes button to turn red, but no action occurs;
  - Second press ② button turns pink and executes the shutdown procedure



# Checking Results

## Analysis Tab

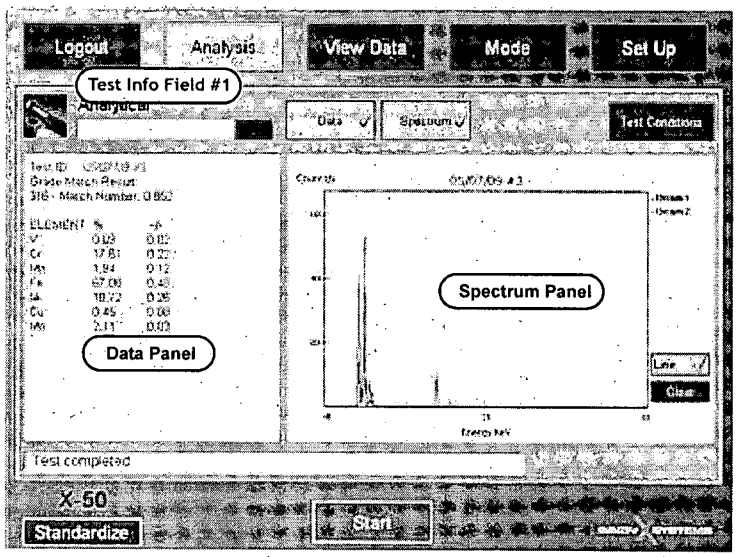
This tab displays the most recent result with the information reported in the data and spectrum panels.

Data panel shows a list of detected elements and their concentrations.

Touch a spectrum graph, the counts rate and energy at that point are displayed.

With the Line button toggled on, a touch on the spectral display shows the elemental energy lines in their appropriate locations.

The Clear button removes the lines.



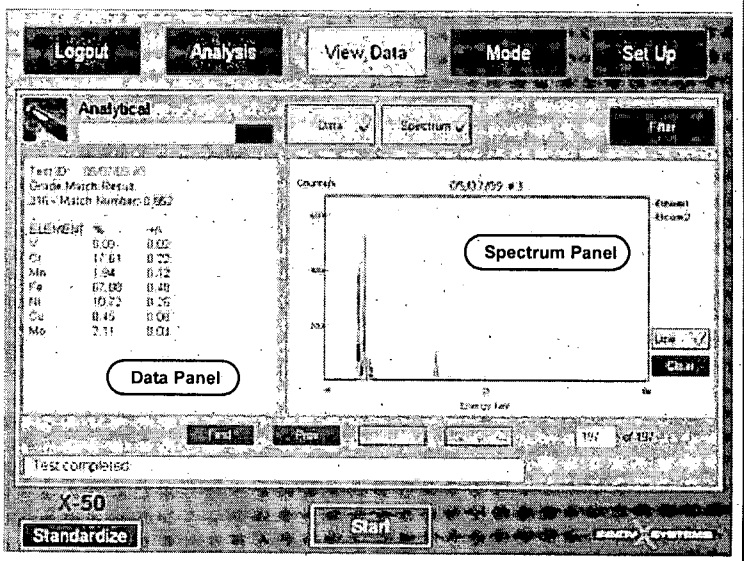

## View Data Tab

Select this tab to view ALL historical test results.

Similar to the Analysis tab, results are reported in the data and spectrum panels.

Navigation buttons allow an operator to examine the entire test results data set.

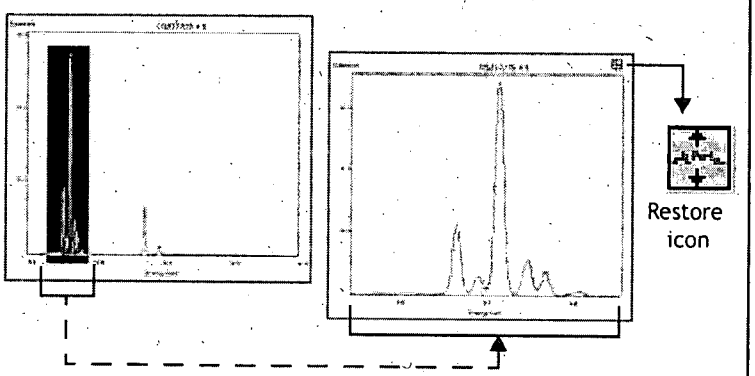
Filter button is a shortcut to the Search Filter screen of the Setup tab.




## TIPS

To expand certain plot areas, use your finger (or mouse) to select one corner and drag out the region of interest.

Press the Restore icon to bring the plot back to full scale.



# 6. Safety Administration

The *X-50* analyzer is a very safe instrument when used according to Innov-X's recommended safety procedures.

- Detectable radiation is below the limit for an uncontrolled area and is within regulatory limits.
- The x-ray tube has a multi-tiered safety interlock structure. See ***Product Safety Features, Page 4***.

Dosimeter

A dosimeter consists of a radiation-sensitive material packaged in a small container like a badge or ring.


Dosimeter
Badge Clip-on Style

Dosimeter
Ring Style

These devices record a person's accumulated radiation exposure over a period of time. It monitors workers using devices which emit ionizing radiation.

- Dosimeter badges are required by some states, and are optional with others.

Innov-X recommends that (at a minimum) all *X-50* analyzer operators wear badges/rings for the first year that their analyzer is in use.

# 7. Specifications

| Component | Description |
|---|---|
| Carry Case and Enclosure | • Rugged carry case with wheels and telescoping handle<br>• Analyzer enclosure is rugged injection molded multi-hinged unit.<br>• Dimensions: Closed — 15/38 H x 12.5/32.8 W x 11/28 D [inches/centimeters]<br>• Dimensions: Open — 18/46 H x 12.5/32.8 W x 27/69 D [See *Page 3* for outline]<br>• Weight: 26 lbs/11 kg |
| Sample Chamber | • Dimensions: 11.3/28.7 W x 5.7/14.5 D x 4.5/11.4 H at front edge of platform.<br>• Lid has safety interlocks that create a closed beam system |
| Power Requirements | • 100 - 240 VAC, 50-60 Hz, auto switching power adapter; maximum draw less than 70 watts |
| Excitation System | • 50 kV, 200 uA X-ray tube |
| Primary Beam Filters | • Six position primary beam filters for optimal performance across the periodic table |
| Detection System | • High purity Si PiN detector delivers < 190 eV resolution |
| Computer | • Pentium processor with Windows® XP Embedded Runtime software; color touchscreen for display, mouse, and keyboard functions. I/O ports for external USB (2), serial, VGA devices, and network access. |
| Operating Environment | • Temperature: 0 - 50°C<br>• Humidity: 10 - 90% Relative Humidity, non-condensing |

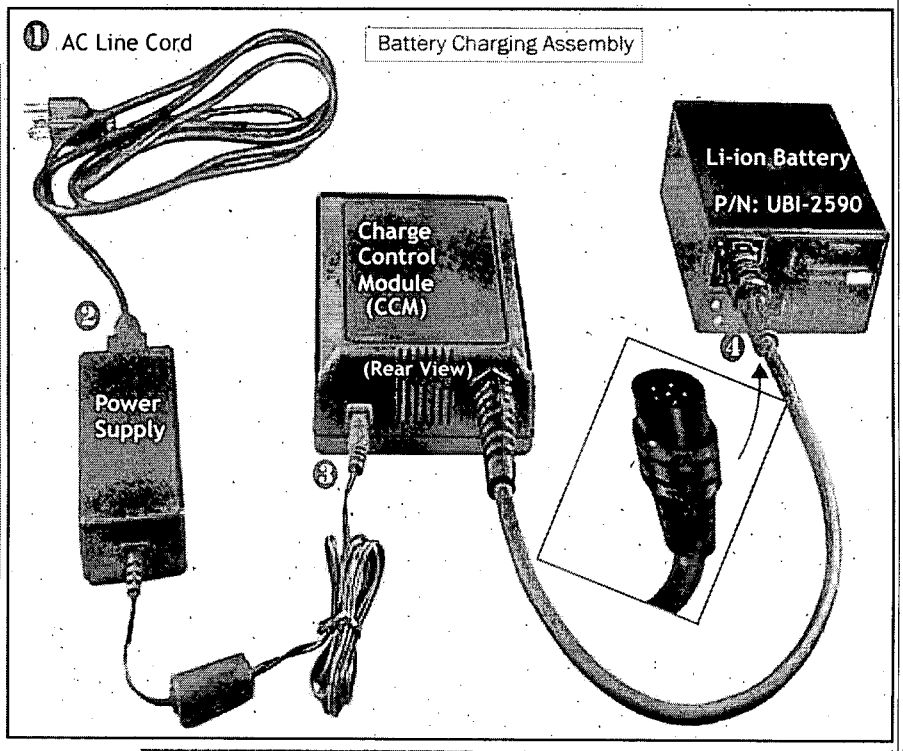
# 8. Battery Option

For complete mobile functionality, the X-50 can be outfitted with a rechargeable military-grade lithium-ion battery.
The battery is initially shipped with a charged condition between 50 and 70% of capacity.

Innov-X recommends that you completely charge the battery as soon as practical. Instructions are shown below. A Charge Control Module (CCM) manages the power to the battery. Charging to 100% takes approximately three hours. The CCM prevents over-charging.

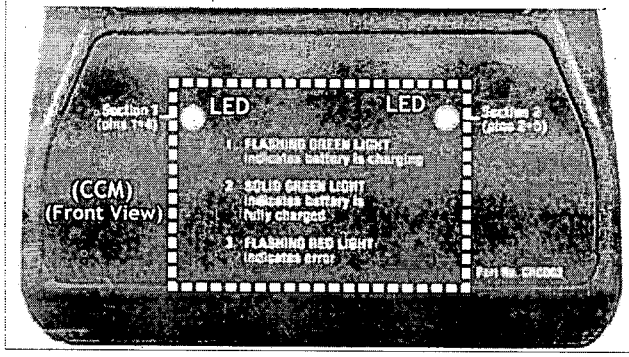
**INSTRUCTIONS:**
**Battery Charging**

1. Plug AC line cord into grounded power source.
2. Insert cord socket into the Power Supply
3. Insert DC Output into Charge Control Module DC Input Socket.
4. Insert CCM DC Output Connector into the Battery Input Socket.
   -Ensure that the pins and guides are aligned.

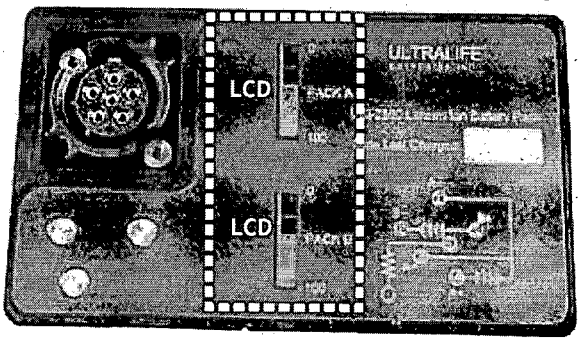



**STATUS:**
**Battery Charge**

Two LED indicators on the front of the CCM show the status of the charging cycle.

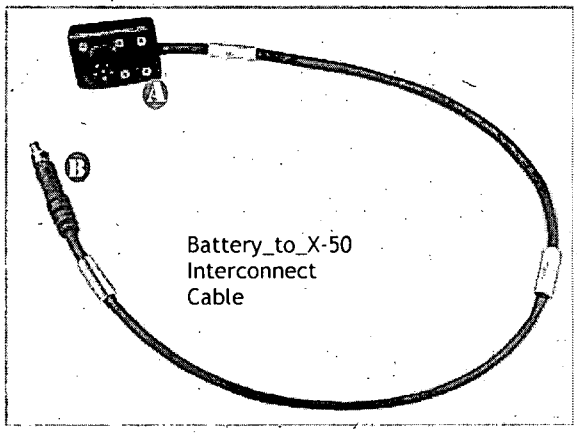



Two LCD indicators on the battery display the percent of capacity now available.



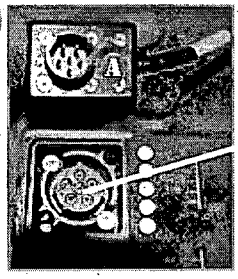
INSTRUCTIONS:
**Battery Connection**

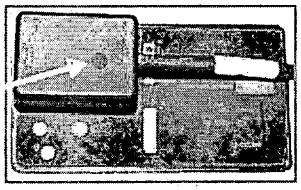
1. Using the Interconnect Cable, plug connector A into battery socket.
2. Lift rubber cover over the X-50 Power socket.
3. Insert DC Output jack B into Power socket.



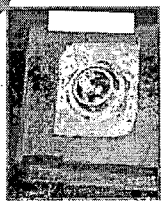

Battery_to_X-50
Interconnect
Cable

1

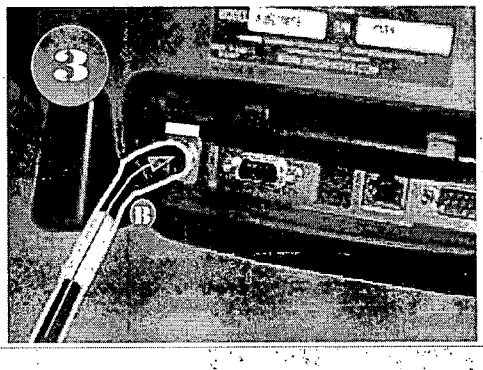


2



3




## WARNING

- NEVER puncture, drop, crush, throw, hit, open, or modify the battery or casing.
- Do NOT incinerate.
- Do NOT submerge this product in water or any liquid.

## CAUTION

When shipping this Li-ion battery, always observe all local transportation regulations.

# 10. Packing and Return Shipping

**If the instrument is not returned in the protective case, it can be damaged during shipping. Innov-X Systems reserves the right to void the warranty on instruments shipped without the protective case that are damaged during shipping. Prior to returning a unit, to receive the required RMA number and to answer any shipping questions, call Customer Service at 781-938-5005.**

Follow these instructions to return your XRF Analyzer:

1. Pack the analyzer in the black protective case in which it arrived, using the original packing materials.
2. Include the RMA in the case and reference the RMA number in your shipping documents.
3. Close the protective case and either:
   - Secure it with plastic zip ties, or
   - Pack the protective case within another box.